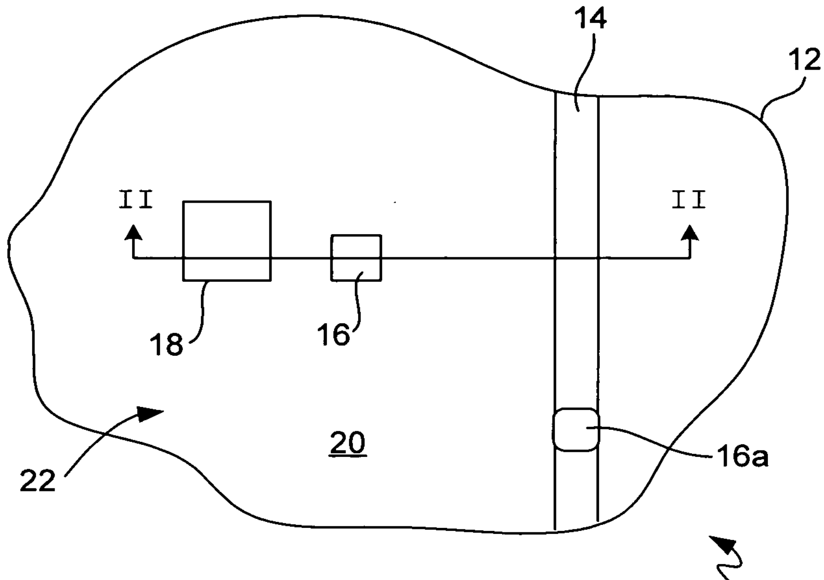

14
12
II
II
18
16
22
20
16a
10

FIG. 1

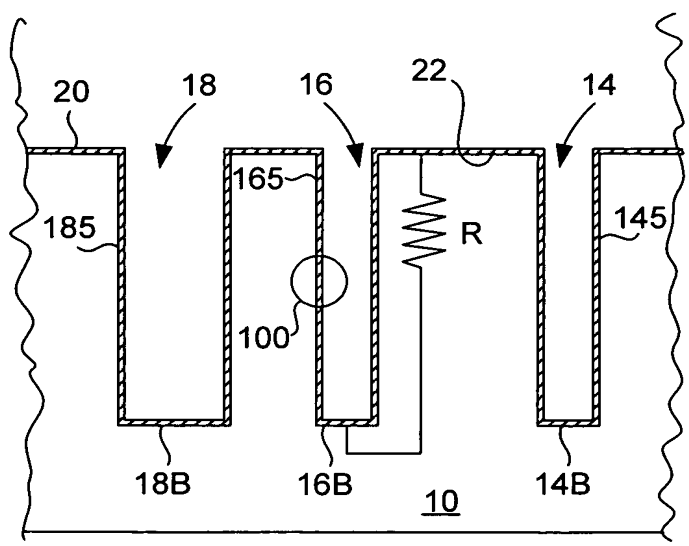

20
18
16
22
14
165
185
R
145
100
18B
16B
10
14B

FIG. 2

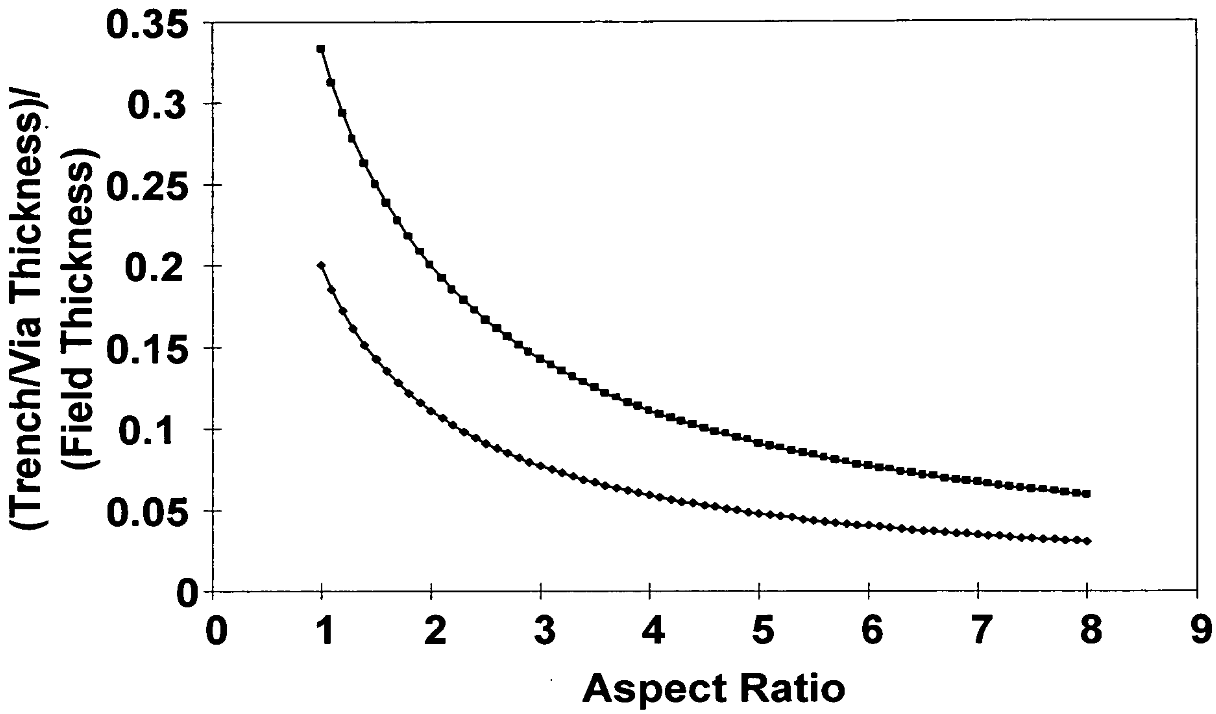

0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
(Trench/Via Thickness)/
(Field Thickness)
0
1
2
3
4
5
6
7
8
9
Aspect Ratio

FIG. 3

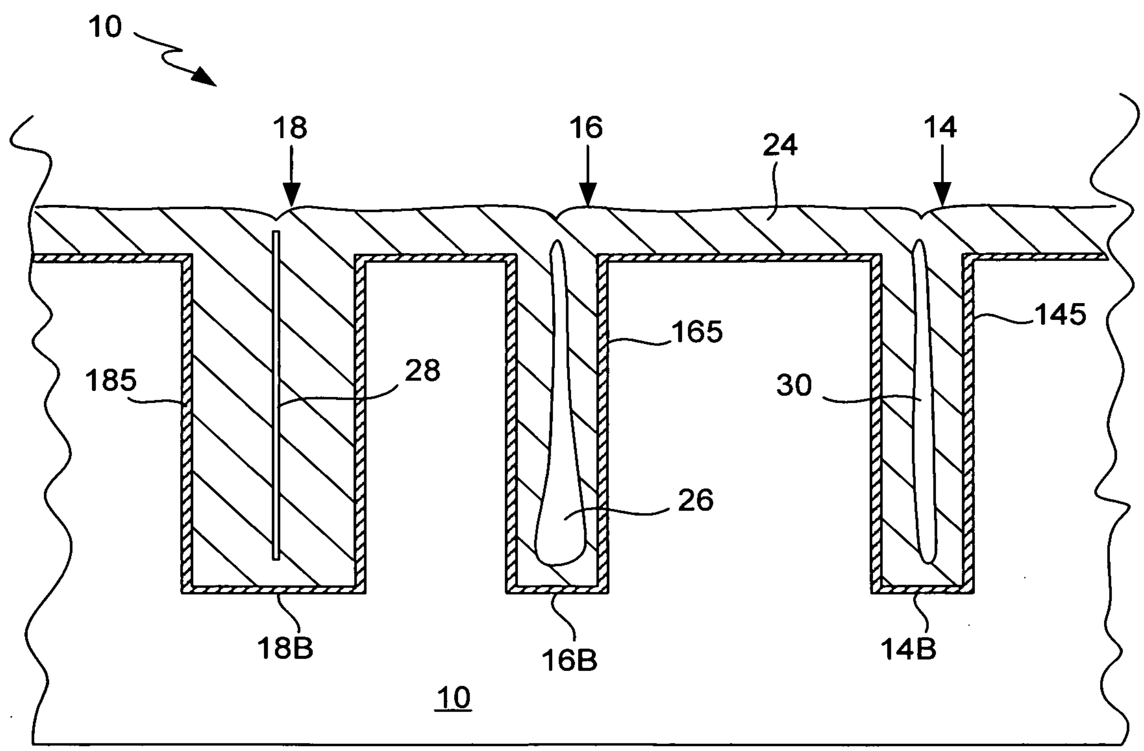

10
18
16
24
14
165
145
185
28
30
26
18B
16B
14B
10

FIG. 4

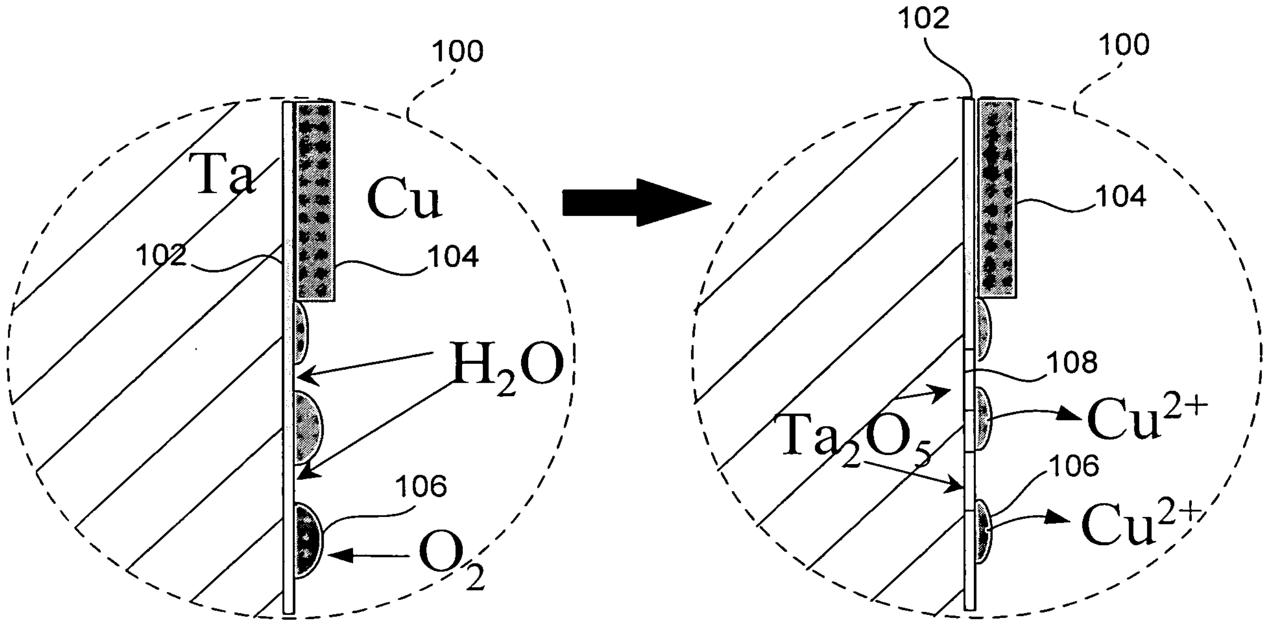


FIG. 5A

FIG. 5B

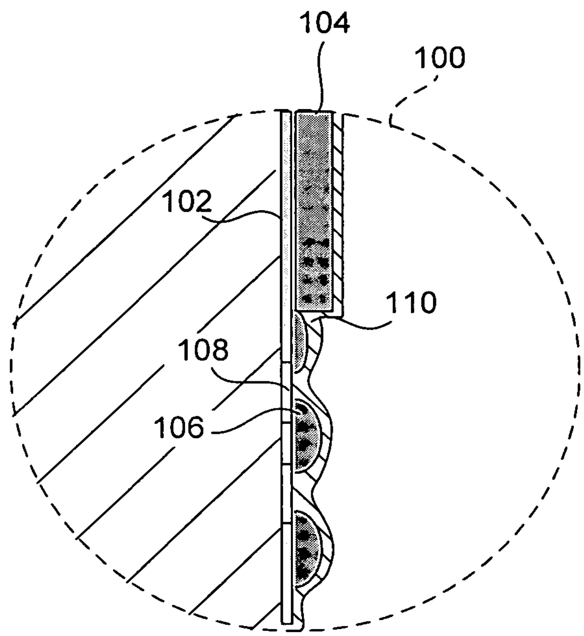


FIG. 6

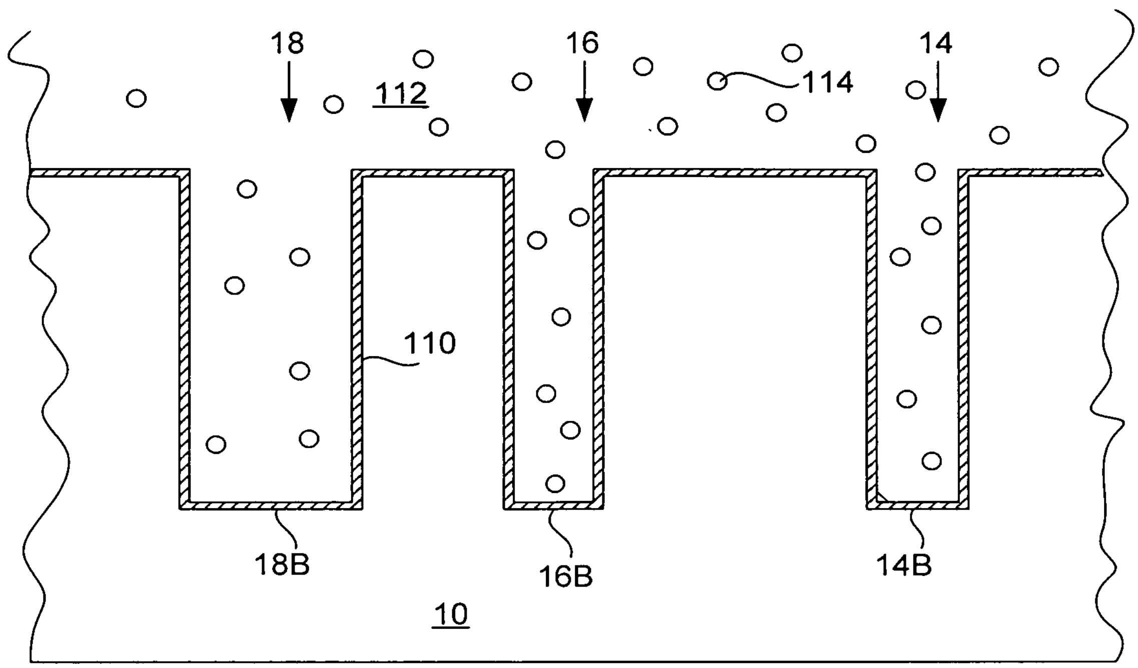


FIG. 7

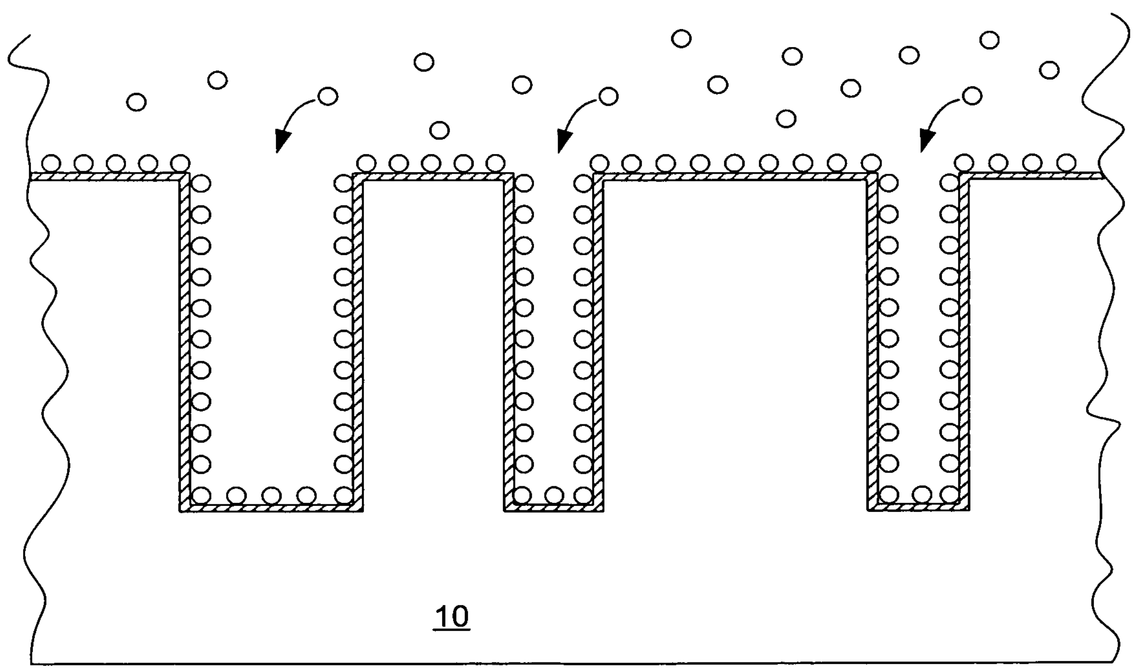


FIG. 8

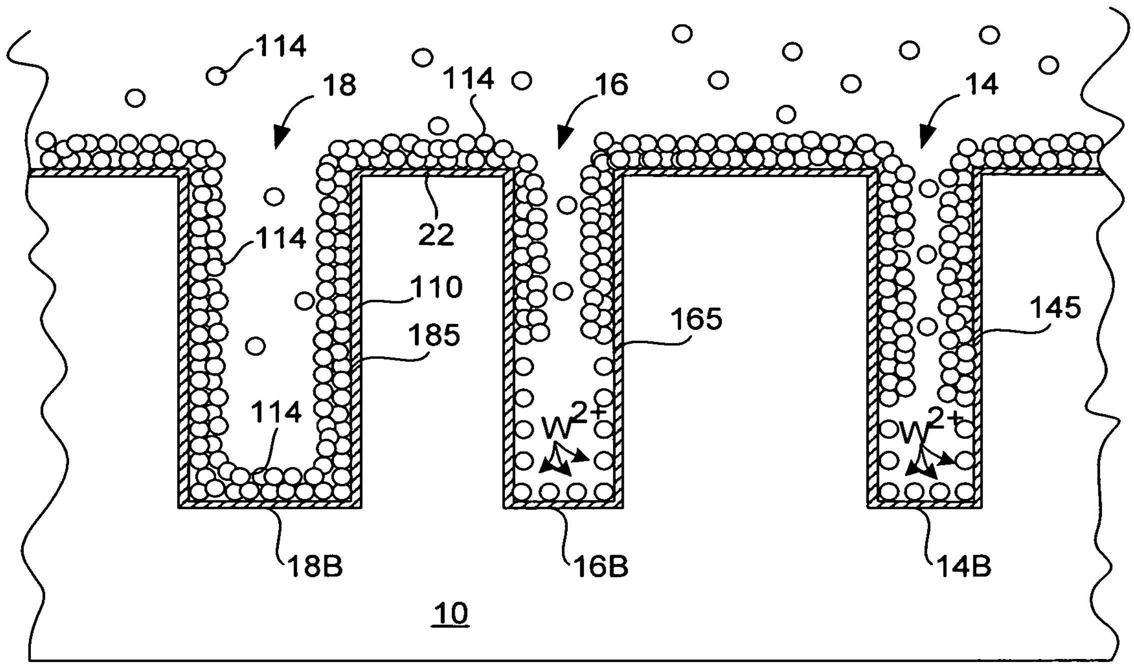

114
18
114
16
14
22
114
110
185
165
145
114
W^{2+}
W^{2+}
18B
16B
14B
10

FIG. 9

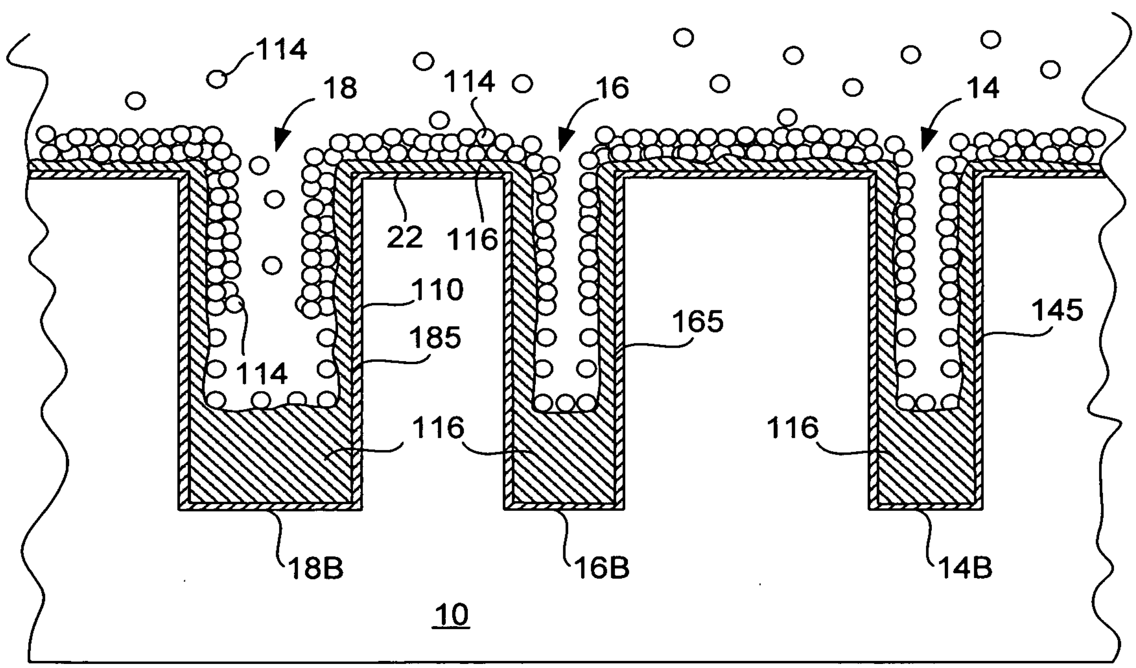

114
18
114
16
14
22
116
110
185
165
145
114
116
116
116
18B
16B
14B
10

FIG. 10

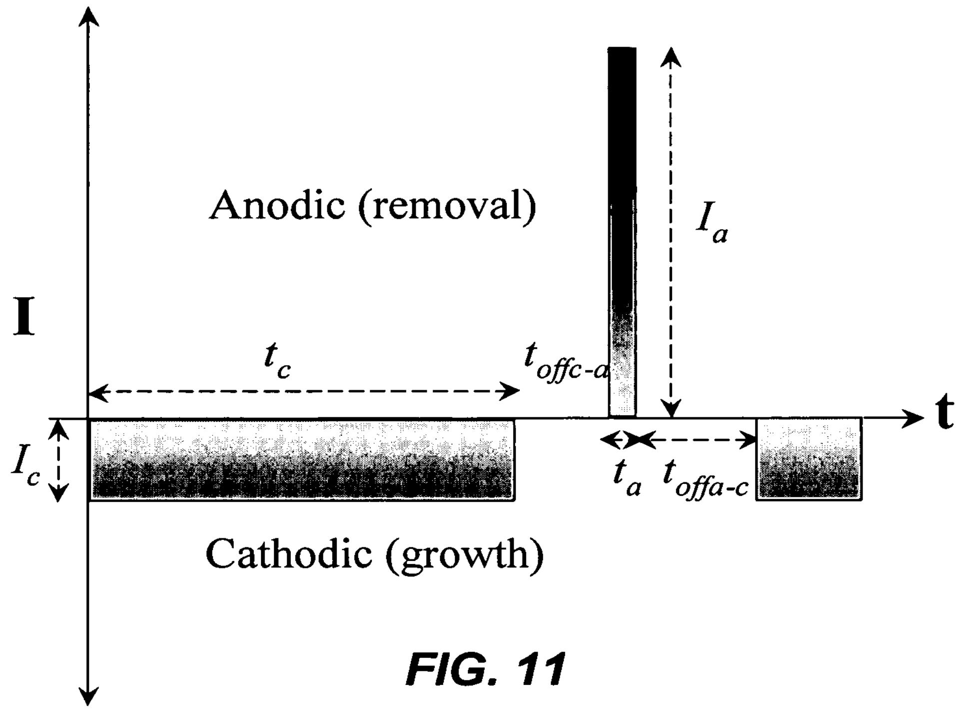

Anodic (removal)
I_a
I
t_c
t_{offc-a}
t
I_c
t_a
t_{offa-c}
Cathodic (growth)

FIG. 11

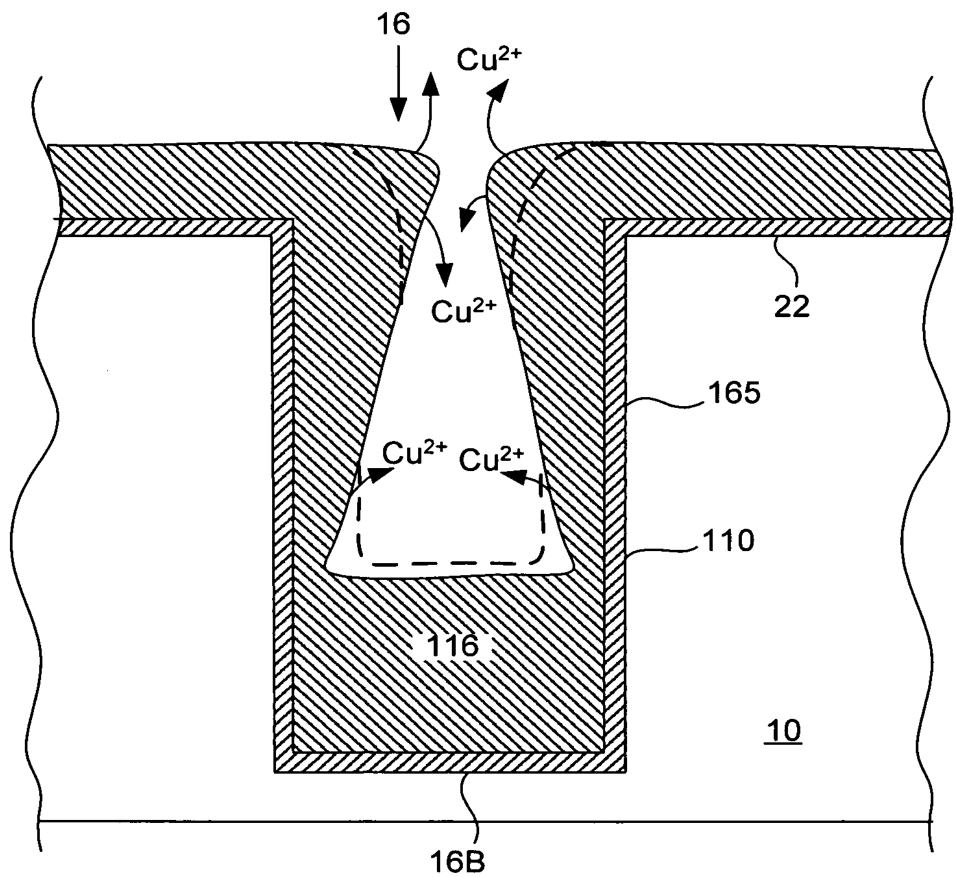

16
Cu^{2+}
Cu^{2+}
22
165
Cu^{2+}
Cu^{2+}
110
116
10
16B

FIG. 12

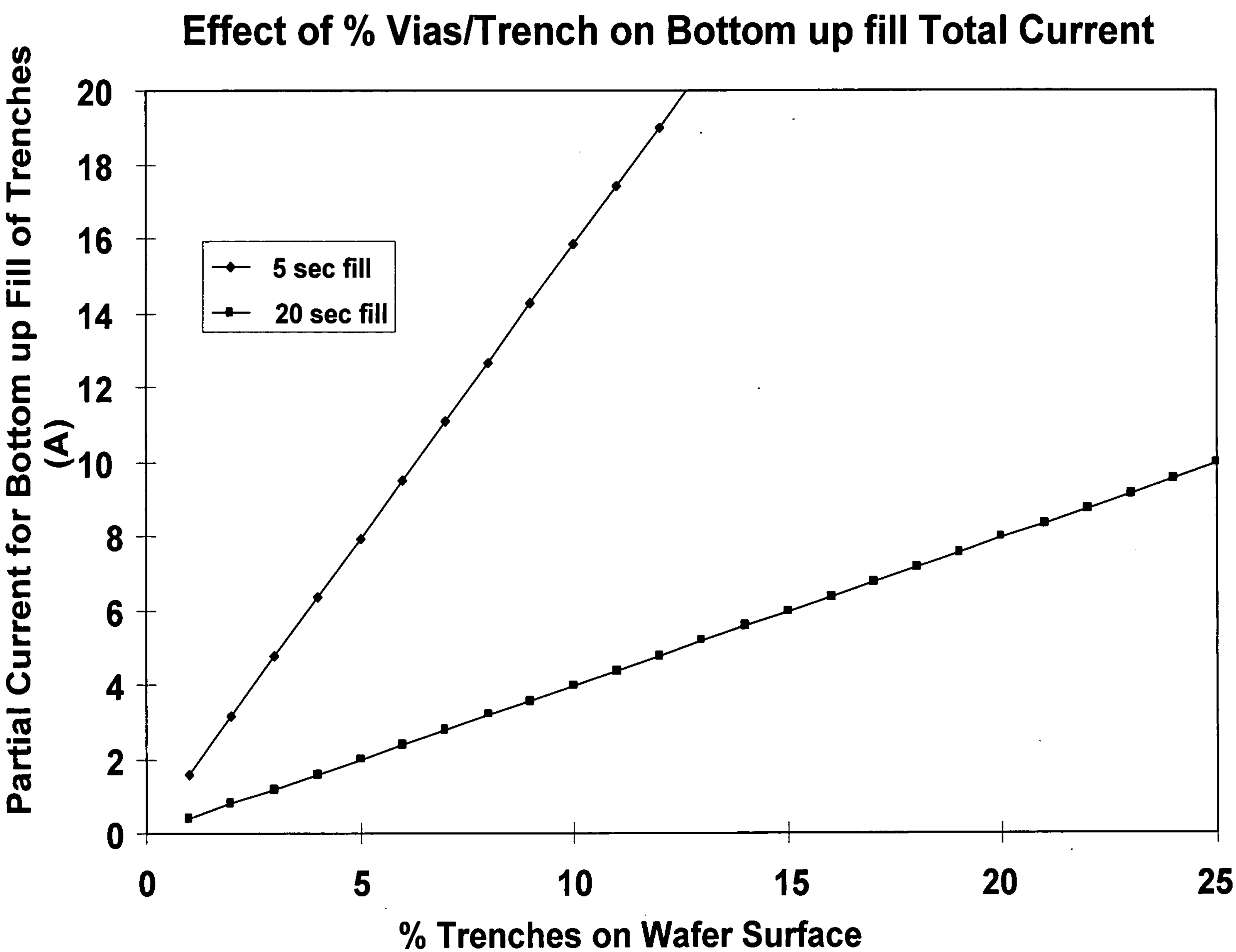
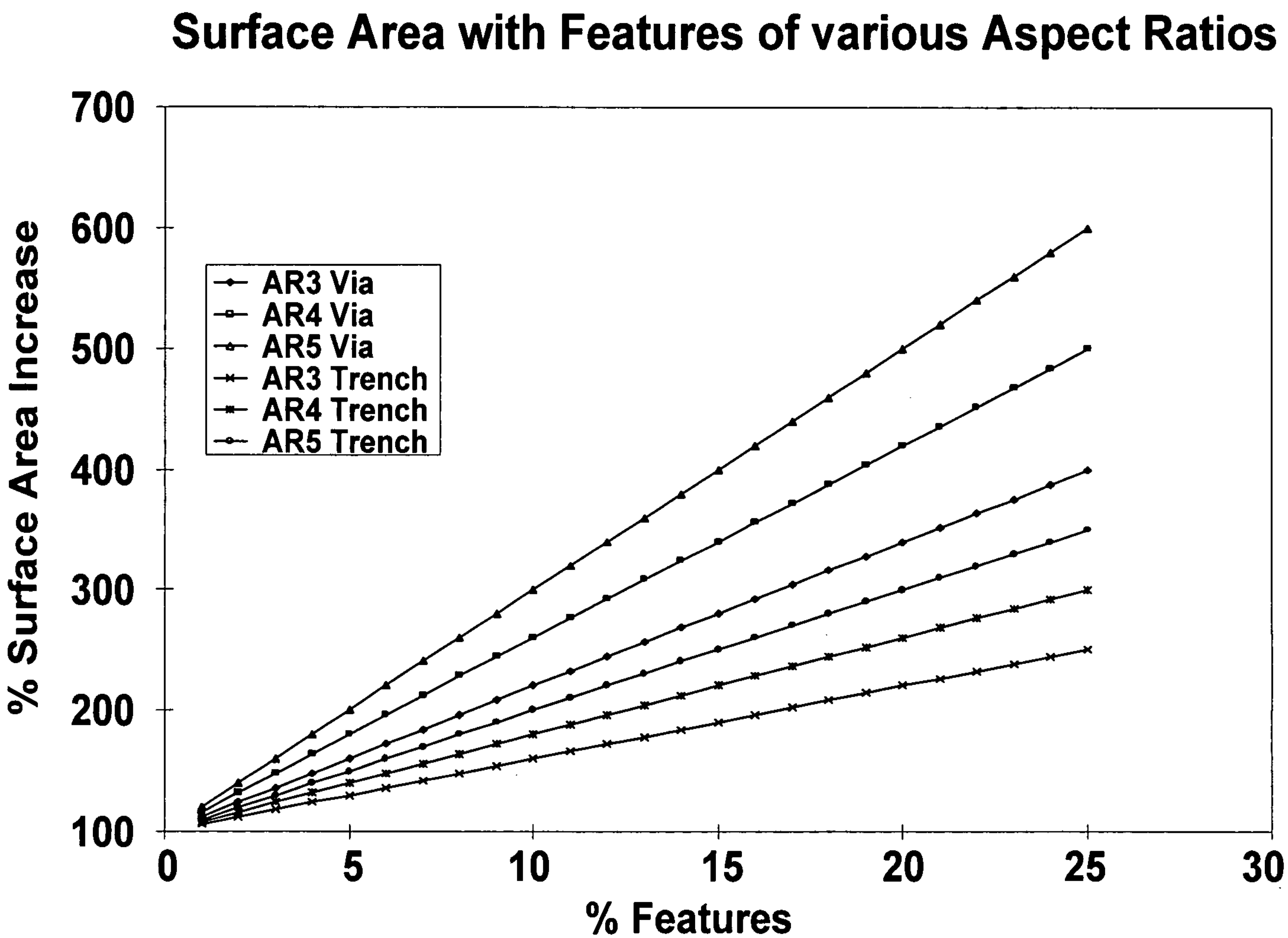

Effect of % Vias/Trench on Bottom up fill Total Current
Partial Current for Bottom up Fill of Trenches (A)
20
18
16
14
12
10
8
6
4
2
0
5 sec fill
20 sec fill
0
5
10
15
20
25
% Trenches on Wafer Surface

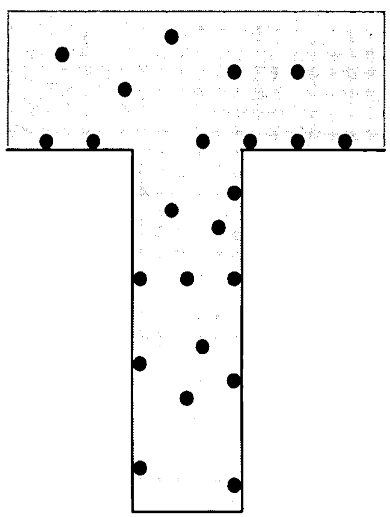
FIG. 13



$$\frac{A_{total}}{A_{wafer}} = f_{field} + \sum_{i=1}^{n} f_i[1+4A] + \sum_{j=1}^{m} f_j[1+2A]$$

FIG. 14

How Much Additive Comes in With the Solution?



Ratio:
Surface to Solution Molecules

Aspect Ratio				
2	299	60	155	52
2.5	365	73	190	63
3	432	86	224	75
3.5	498	100	259	86
4	565	113	293	98
4.5	631	126	327	109
5	697	139	362	121
5.5	764	153	396	132

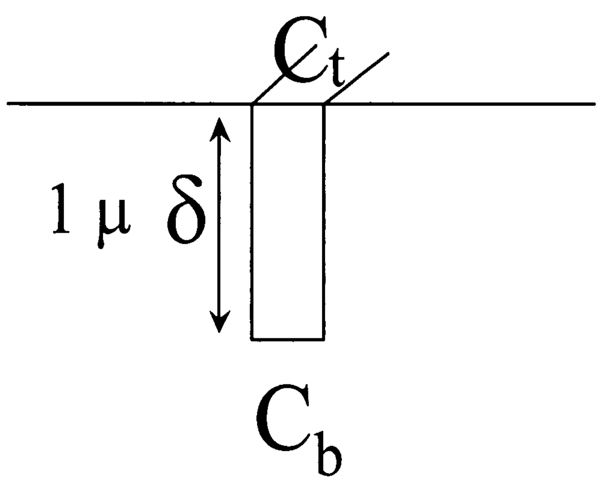
Conditions				
ppm	20	100	100	300
MW	100	100	3000	3000
Moles/um^3	2.0E-19	1.0E-18	3.3E-20	1E-19
Molec/um^3	120460	602300	20077	60230
Molecules size (nm)	0.5	0.5	1.7	1.7
Molec/um^2	4000000	4000000	346021	346020.8

Conclusion: At all expected additive condition, there is insufficent material stored in the inital solution within the via to lead to substantial surface absorption in the via.

-There will be an absorption time delay.

FIG. 15

Time Estimate for Plating Additives Absorption



Assumptions

1. Inital surface coverage is zero
2. Final surface coverage is $1x10^{15}$ molecules/cm^2 (1 monolayer).
3. Very fast absorption kinetics (diffusion controlled)
4. No side wall absorption

$$\Delta C = 10ppm = 5.5x10^{-8}\ M / cm^3$$

$$\delta = 1\mu = 1.0x10^{-4}\ cm$$

$$D = 1.0x10^{-6}\ cm^2 / \sec$$

Conclusions

1. Diffusion controled absorption inside of trench take a few seconds.
2. Larger surface area of trench will increase this time from this estmate.
3. High additive level will decrease time estimate

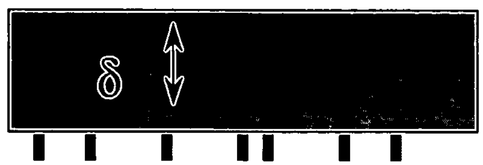
$$F = \frac{D\Delta C}{\delta} = 5x10^{-10}\ M / \sec cm^2 = 3.4x10^{14} molecules / \sec cm^2$$

$$t_{abs} = 1x10^{-15} molecules / cm^2 / 3.4x10^{14} molecules / \sec cm^2 = 2.9 \sec$$

FIG. 16

Time Estimate for Absorption of Plating Additives

Assumptions



1. Inital surface coverage is zero everywhere
2. Final surface coverage is $1x10^{15}$ molecules/cm^2 (1 monolayer).
3. Very fast absorption kinetics (diffusion controlled)
4. Concentraton at edge of boundary layer is bulk

$$\Delta C = 10 ppm = 5.5x10^{-8}\ M / cm^3$$
$$\delta = 5.7\mu = 5.7x10^{-4}\ cm$$
$$D = 1.0x10^{-6}\ cm^2 / \sec$$

Conclusions

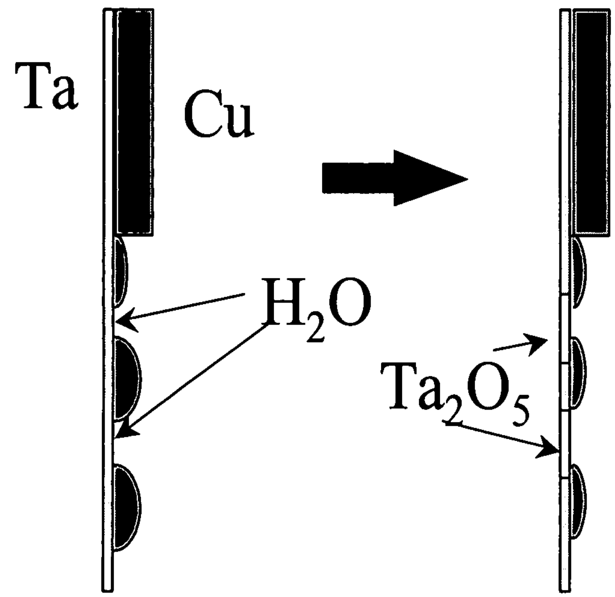
Diffusion of very low concentration plating additives may take several seconds to occur

$$F = \frac{D\Delta C}{\delta} = 1x10^{-10}\ M / \sec cm^2 = 0.7x10^{14} molecules / \sec cm^2$$

$$t_{abs} = 1x10^{-15} molecules / cm^2 / 0.7x10^{14} molecules / \sec cm^2 = 14 \sec$$

FIG. 17

How Would Ta_2O_5 be Formed in the Side Walls?

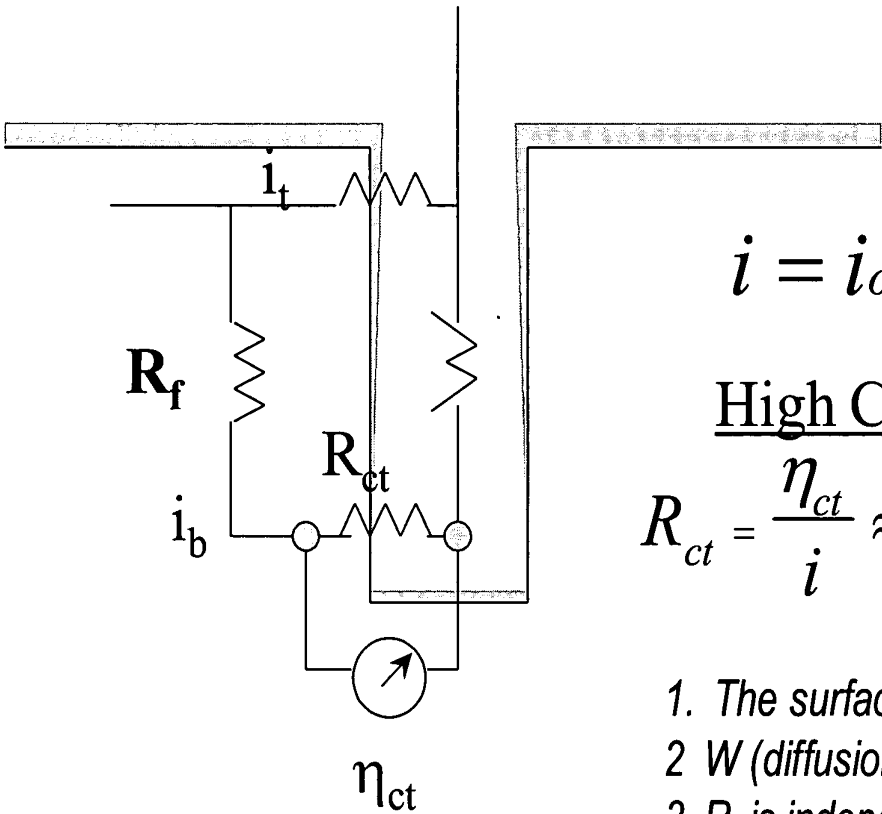


$$
\begin{array}{lll}
2Ta + 5H_2O & Ta_2O_5 + 10H^+ + 10\,e^- & E_o = -0.75V \\
10\,H^+ + 10\,e^- & 5H_2 & E_o = 0.00\ V \\
\hline
2Ta + 5H_2O & Ta_2O_5 + 5H_2 & \Delta E = 0.75V
\end{array}
$$

<u>Conclusions:</u>	Formation of Ta_2O_5 is anticipated (thermodynamics)’
<u>Question:</u>	How much of the Ta is expected to be converted to the electrically insulating oxide?

FIG. 18

Equivalent Circuit Model of Via/Trench Filling



$$i = i_o\left[e^{-\alpha n f \eta_{ct}} - e^{(1-\alpha) n f \eta_{ct}}\right]$$

<u>High Current</u>

$$R_{ct} = \frac{\eta_{ct}}{i} \approx \frac{\eta_{ct}}{i_o e^{-\alpha n f \eta_{ct}}}$$

<u>Low Current</u>

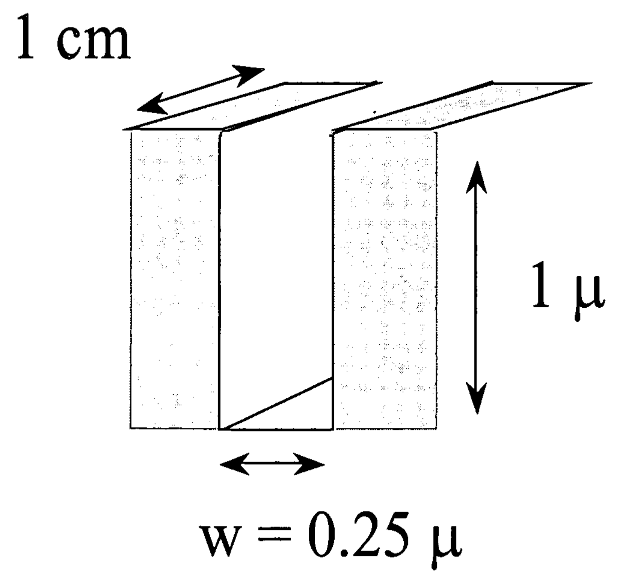
$$R_{ct} = \frac{\eta_{ct}}{i} \approx \frac{1}{i_o n F}$$

1. *The surface resistance **increases** with decreasing current !*
2 *W (diffusion resistance) increases with increasing current*
3. *R_f is independant of current*

When is R_f significant ?

FIG. 19

Electrical Resistances and Filling of Small Features



$$R = \frac{\rho L}{2A} = 4\,m\Omega, 50\,k\Omega$$

$$\Delta V = IR = (iw)R$$

ΔV_{Ta}= 1x10^{-9} to 5x10^{-6} V

ΔV_{Ta2O5}= 0.003 to 0.16 V

Assumptions

1. Only Ta or TaO_2 (2 nm thick) is present on side wall for electrical conductivity
2. Plating occurs only at bottom of trench at 10-500 mA/cm^2 (conformal vs fast bottom-up fill rates).

$\rho_{T\alpha} = 16 \times 10^{-6}\ \Omega$ cm, $\rho_{T\alpha 2O5} = 50\ \Omega$ cm

Conclusions

1. If sidewall metallic Ta of 2 nm is present in the feature, electrical resistivity is insignificant.
2. If sidewall material is cracked, exposed to oxygen and converted to TaO_2, the electrical resistance in the film will be to large to support bottom-up filling.

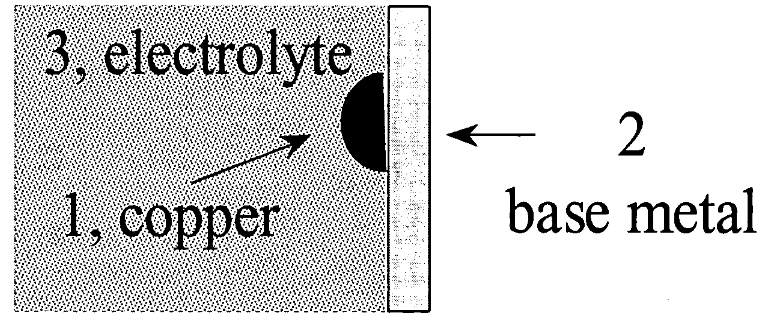
FIG. 20

Nucleation Phenomena

$$\Delta G_t = \pi r^2(2\sigma_{13} + \sigma_{12} - \sigma_{23}) + \frac{2}{3}\pi r^3 \Delta G_v$$

$$\frac{\Delta G_t}{v_m} = \frac{3\ (2\sigma_{13} + \sigma_{12} - \sigma_{23})}{2 v_m r} + \Delta \overline{G}_v$$

$$E(r) = \frac{RT}{nF}\ln\left[\frac{3\ (2\sigma_{13} + \sigma_{12} - \sigma_{23})}{2 v_m r} + \Delta G_v\right]$$



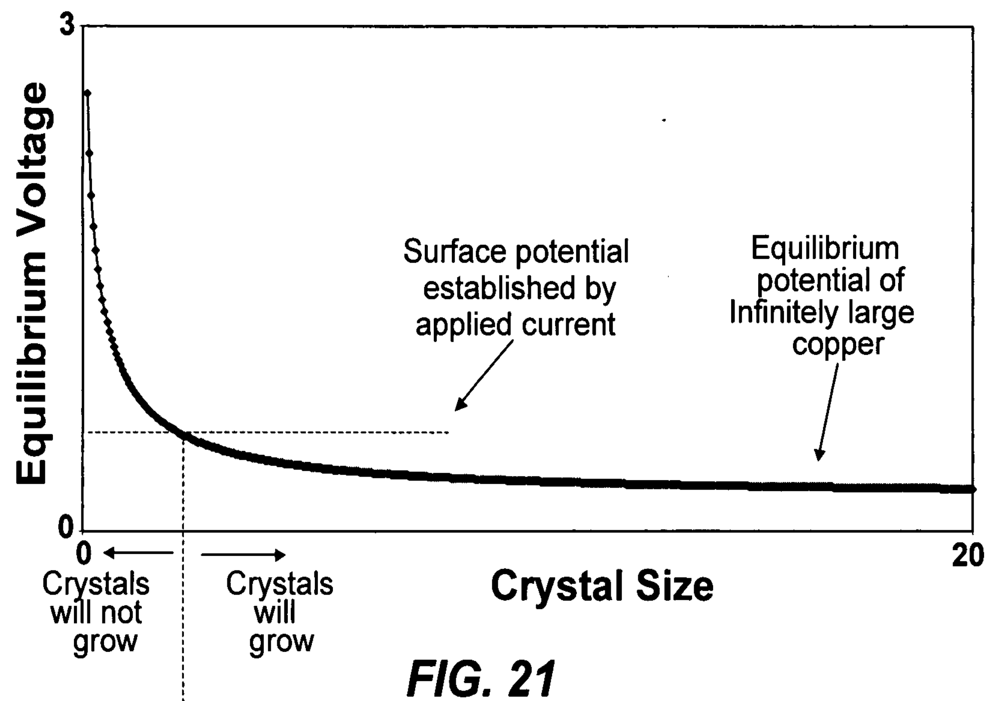
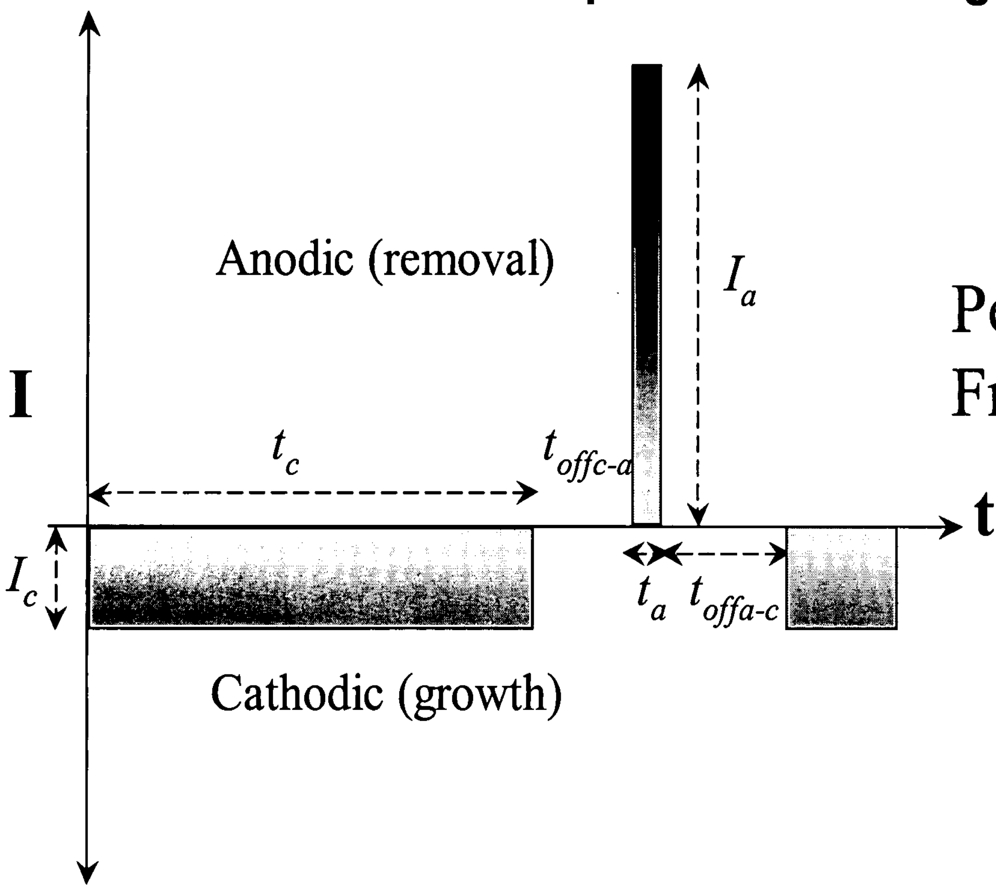


FIG. 21

Bipolar Pulse Plating Waveform



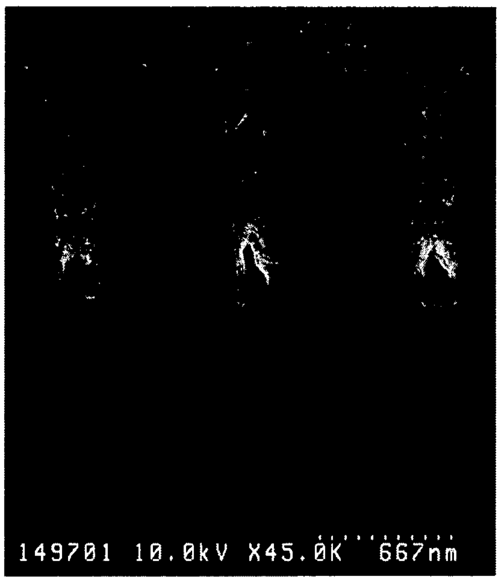
$$\text{Period} = t_c + t_a + t_{offc\text{-}a} + t_{offa\text{-}c}$$
$$\text{Frequency} = 1/\text{Period}$$

$$\text{Constraint: } I_c \,.\, t_c - I_a \,.\, t_a > 0$$

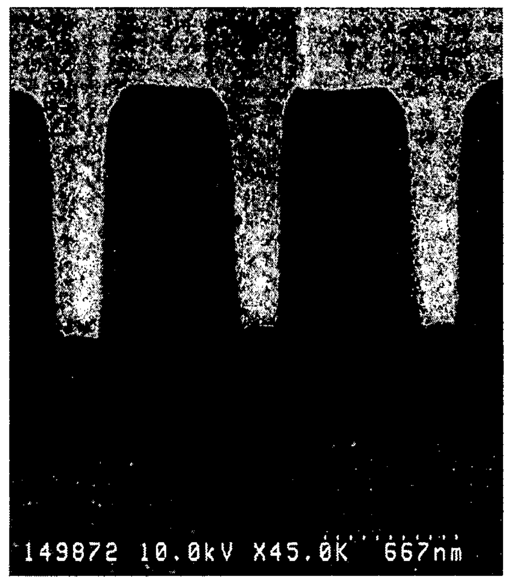
FIG. 22

Bipolar pulse plating: Phase 1-waveform screening

- Select tests done on SEMATECH backfilled vias (Apr 98, 3)
- Bipolar pulse with hi anodic current showed improvement over POR
- Eliminated other pulse waveforms



POR 1.0, 7A DC



10A Cathodic, 80 A Anodic, 125 Hz, 10 msec t_{off}

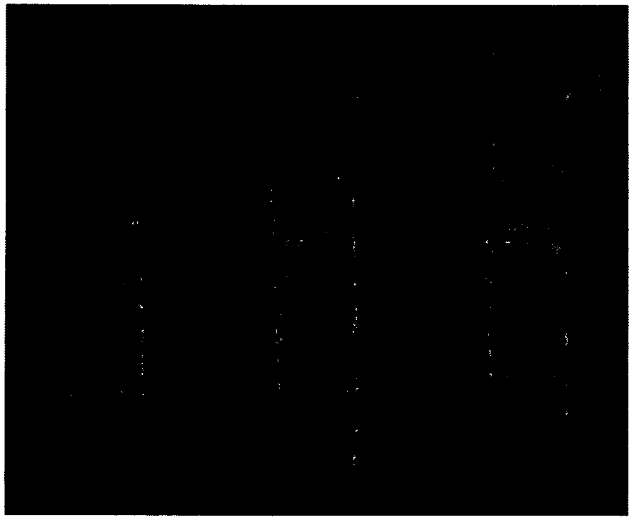
FIG. 23

Bipolar pulse plating: Phase2-Trench optimization

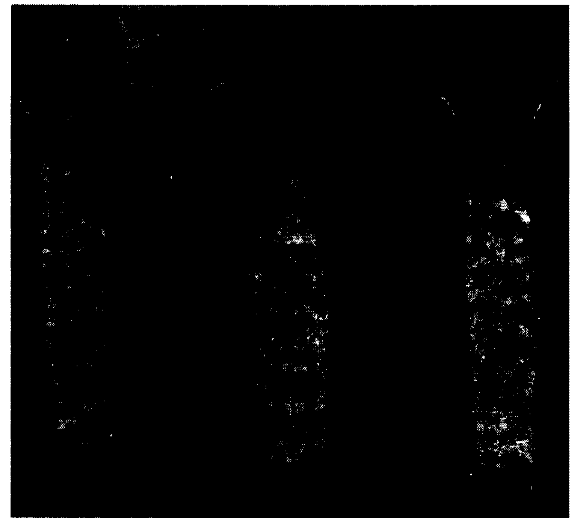
- 1”x1” SEMATECH backfilled trenches with HCM-α seed taped on 8” wafers (52)
- 2 types of waveforms tested
- No pulsed waveform resulted in better fill than POR 1.0
- Higher pulsed anodic currents improved top filling
- Lower pulsed cathodic current improved filling
  - longer on-times were better
- Need to perform tests <u>with</u> initiation on <u>vias</u>

FIG. 24

Fill Improvement: Reverse pulse matrix



A



B

Field 5, 0.34 μm, AR = 4.5

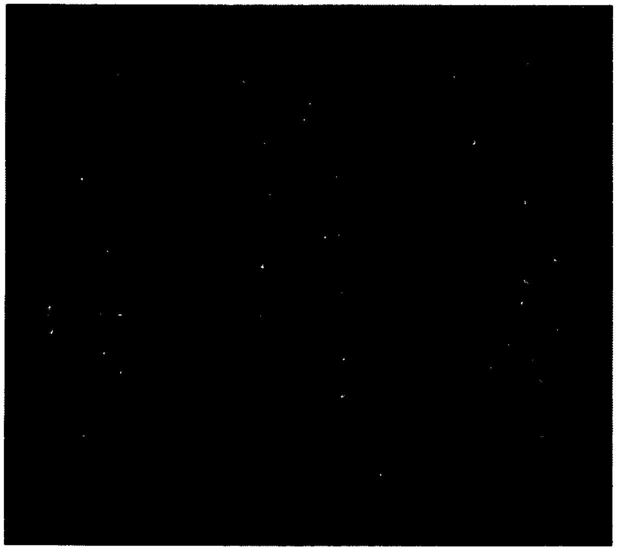
Control, 7A DC

Pulse Matrix				
#	Ic	t_c/t_a ratio	Freq (Hz)	Toff
A	4	25	10	*0*
B	4	25	10	*3*

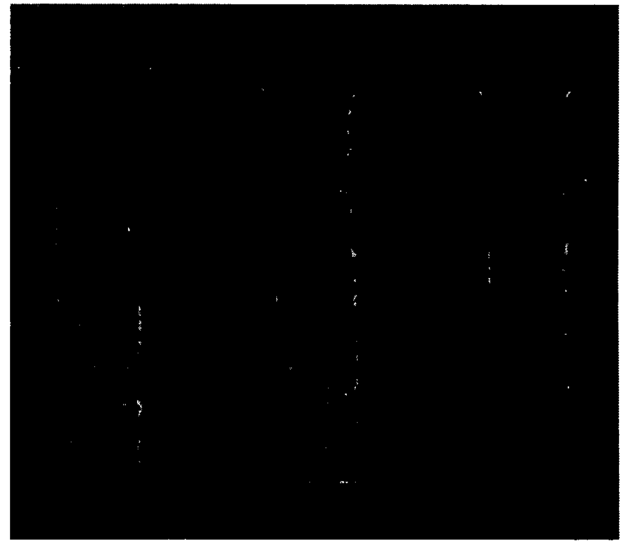
- *Feature*: SEMATECH Standard vias
- *Seed*: 1600Å HCM Cu/250Å HCM Ta
- *Plate*: Step 1: 0.25A DC, 50 sec
  Step 2: Pulse

FIG. 25

Fill Improvement: Reverse pulse matrix



A



B

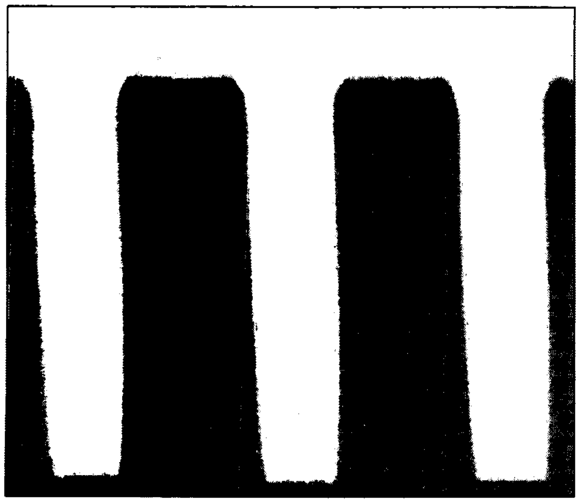
Control, 7A DC

Pulse Matrix				
#	Ic	t_c/t_a ratio	Freq (Hz)	Toff
A	4	24	100	*0*
B	4	22	100	*3*

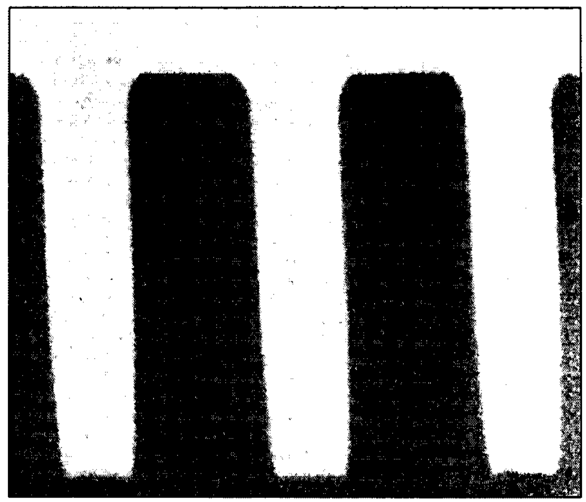
- *Feature*: SEMATECH Standard vias, Field 5, 0.34 μm, AR = 4.5
- *Seed*: 1600Å HCM Cu/250Å HCM Ta
- *Plate*: Step 1: 0.25A DC, 50 sec
  Step 2: Pulse

FIG. 26

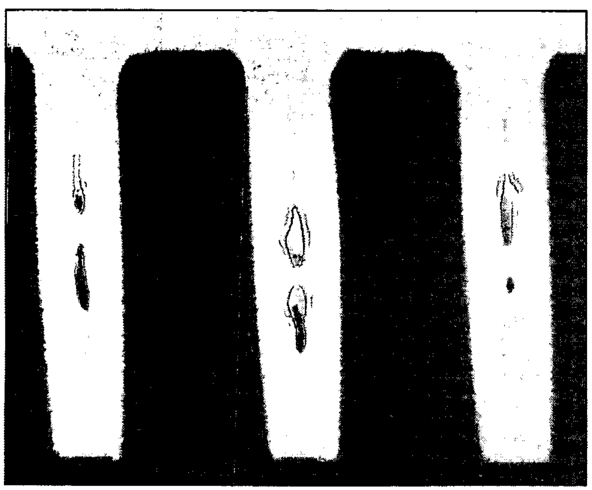
Reverse pulse matrix: Impact of t_c/t_a ratio/freq.



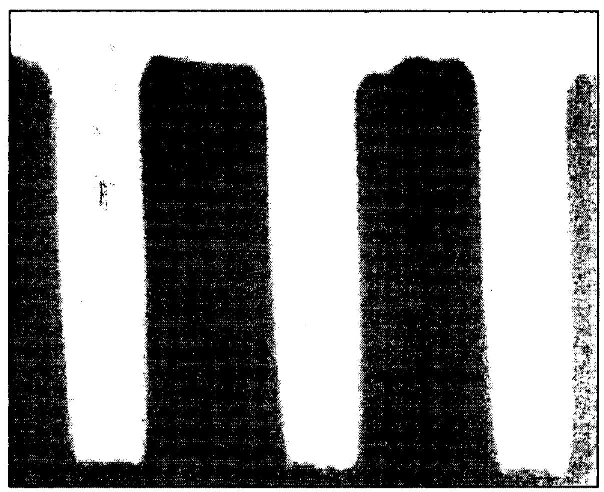
A



B



C



D

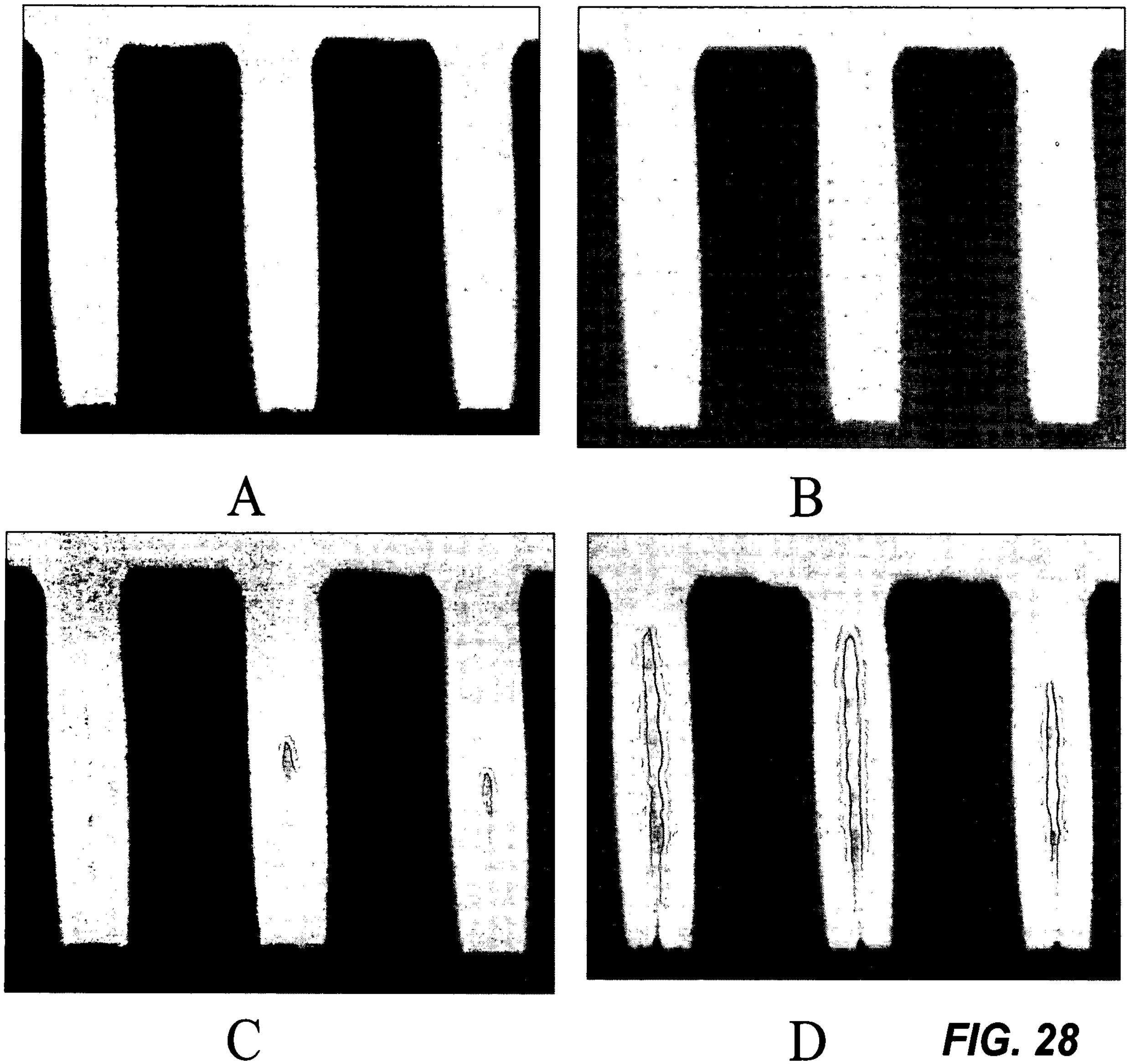
•***Feature***: SEMATECH Standard vias, Field 5, **0.34 μm, AR = 4.5**
•***Seed***: 1600Å HCM Cu/250Å HCM Ta
•***Plate***: Step 1: 0.25A DC, 50 sec
Step 2: Pulse

Pulse Matrix

#	Ic	t_c/t_a ratio	Freq (Hz)	Toff
A	4	*25*	*10*	0
B	4	*25*	*100*	0
C	4	*49*	*10*	0
D	4	*49*	*100*	0

FIG. 27

Reverse pulse matrix: Impact of t_c/t_a ratio/freq.

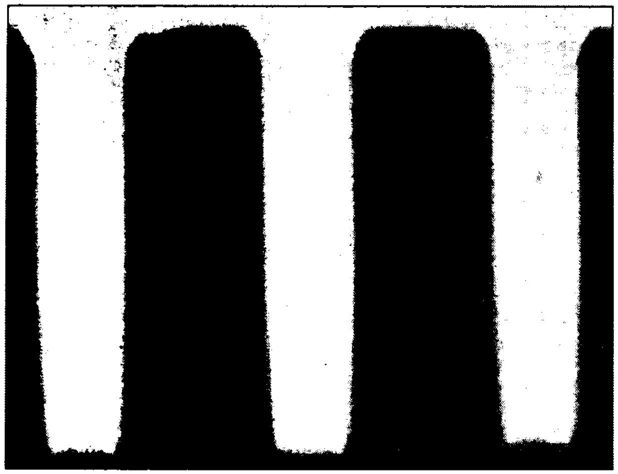


•***Feature***: SEMATECH Standard vias, Field 5, **0.34 µm, AR = 4.5**
•***Seed***: 1600Å HCM Cu/250Å HCM Ta
•***Plate***: Step 1: 0.25A DC, 50 sec
Step 2: Pulse

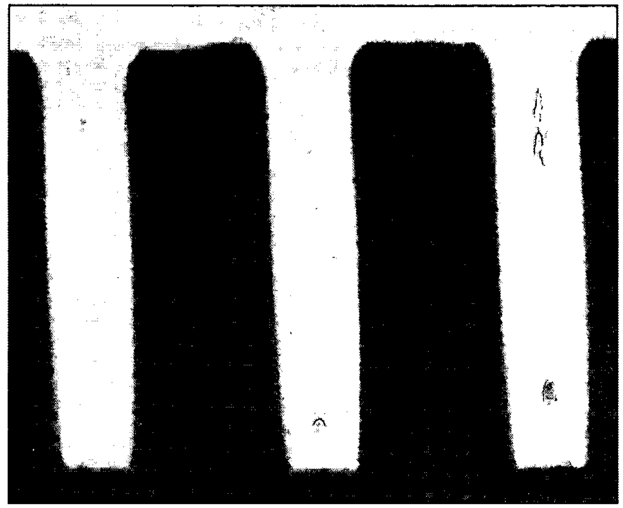
Pulse Matrix				
#	Ic	t_c/t_a ratio	Freq (Hz)	Toff
A	4	*25*	*10*	3
B	4	*25*	*100*	3
C	4	*49*	*10*	3
D	4	*49*	*100*	3

FIG. 28

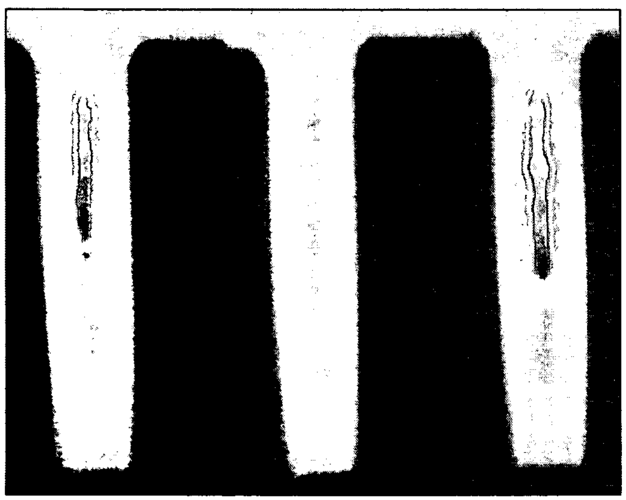
Reverse pulse matrix: Impact of t_c/t_a ratio



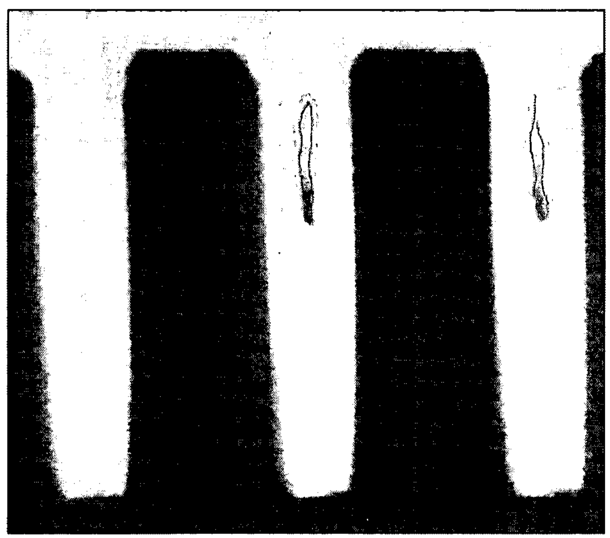
A



B



C



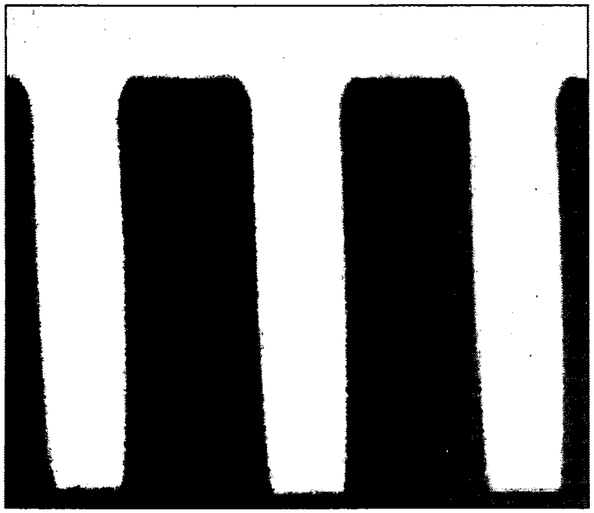
D

FIG. 29

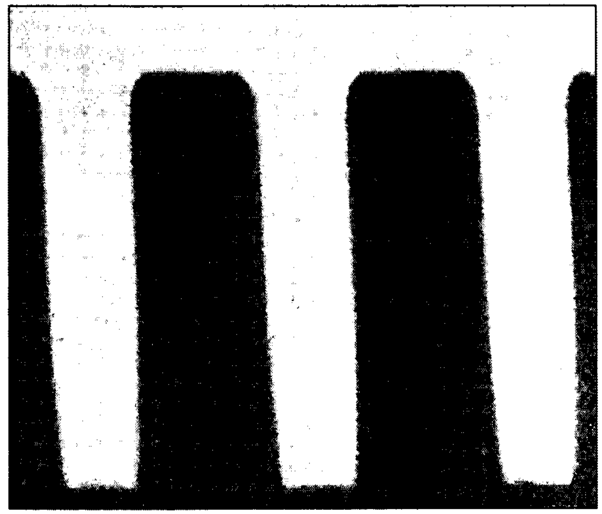
•***Feature***: SEMATECH Standard vias, Field 5, **0.34 µm, AR = 4.5**
•***Seed***: 1600Å HCM Cu/250Å HCM Ta
•***Plate***: Step 1: 0.25A DC, 50 sec
Step 2: Pulse

Pulse Matrix				
#	**Ic**	**t_c/t_a ratio**	**Freq (Hz)**	**Toff**
C	8	***25***	10	***0***
D	8	***25***	10	***3***
C	8	***49***	10	***0***
D	8	***50***	10	***3***

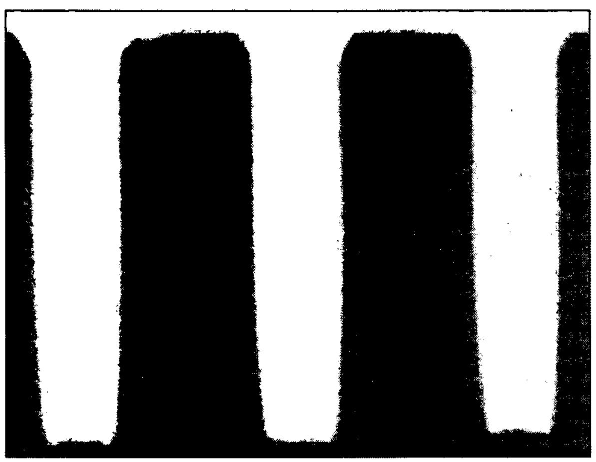
Reverse pulse matrix: Impact of cathodic current/freq.



A



B



C

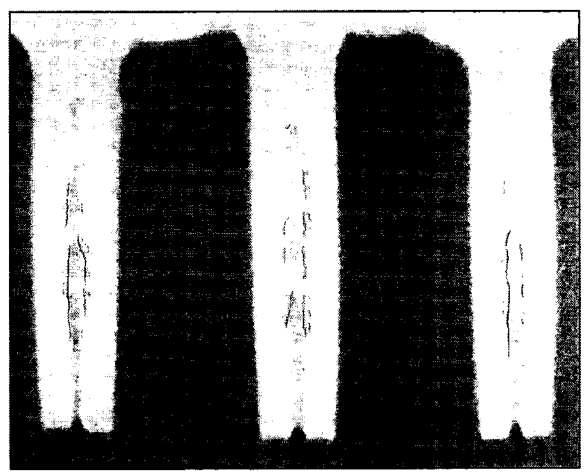


FIG. 30 D

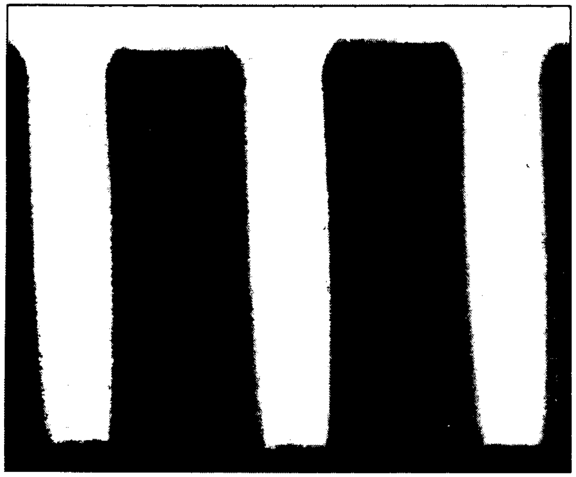
- ***Feature***: SEMATECH Standard vias, Field 5, **0.34 μm, AR = 4.5**
- ***Seed***: 1600Å HCM Cu/250Å HCM Ta
- ***Plate***: Step 1: 0.25A DC, 50 sec

  Step 2: Pulse

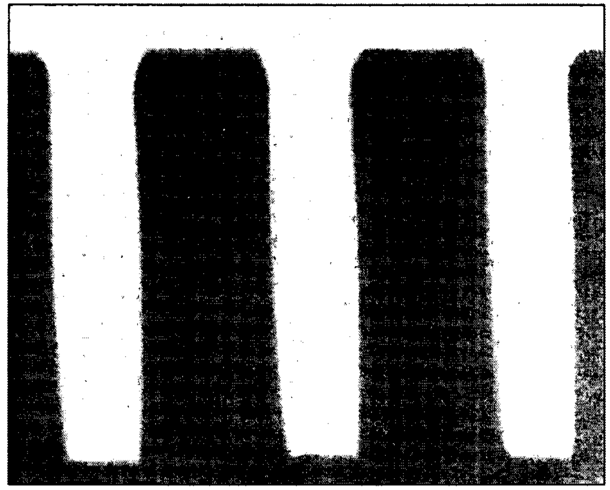
Pulse Matrix

#	Ic	t_c/t_a ratio	Freq (Hz)	Toff
A	*4*	25	*10*	0
B	*4*	25	*100*	0
C	*8*	25	*10*	0
D	*8*	25	*100*	0

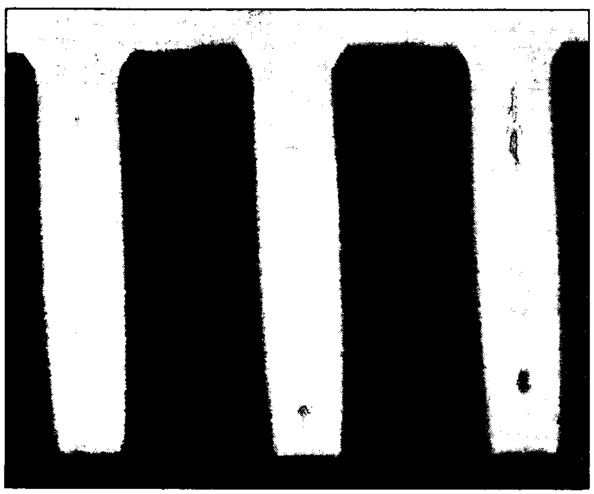
Reverse pulse matrix: Impact of cathodic current/freq.



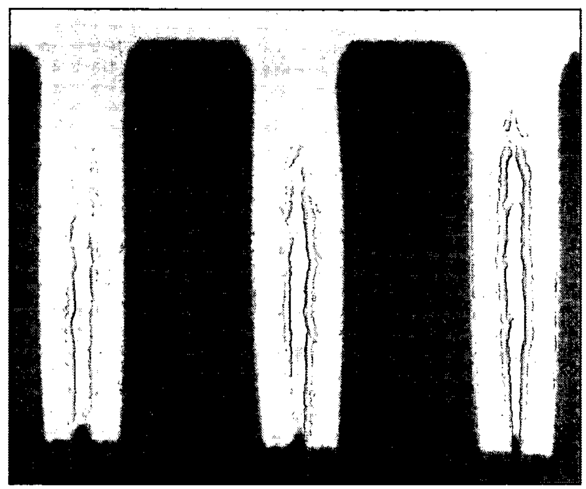
A



B



C



D

FIG. 31

•***Feature***: SEMATECH Standard vias, Field 5, **0.34 μm, AR = 4.5**
•***Seed***: 1600Å HCM Cu/250Å HCM Ta
•***Plate***: Step 1: 0.25A DC, 50 sec
Step 2: Pulse

Pulse Matrix

#	Ic	t_c/t_a ratio	Freq (Hz)	Toff
A	*4*	25	*10*	3
B	*4*	25	*100*	3
C	*8*	25	*10*	3
D	*8*	25	*100*	3

Reverse pulse matrix: impact of cathodic current/off time

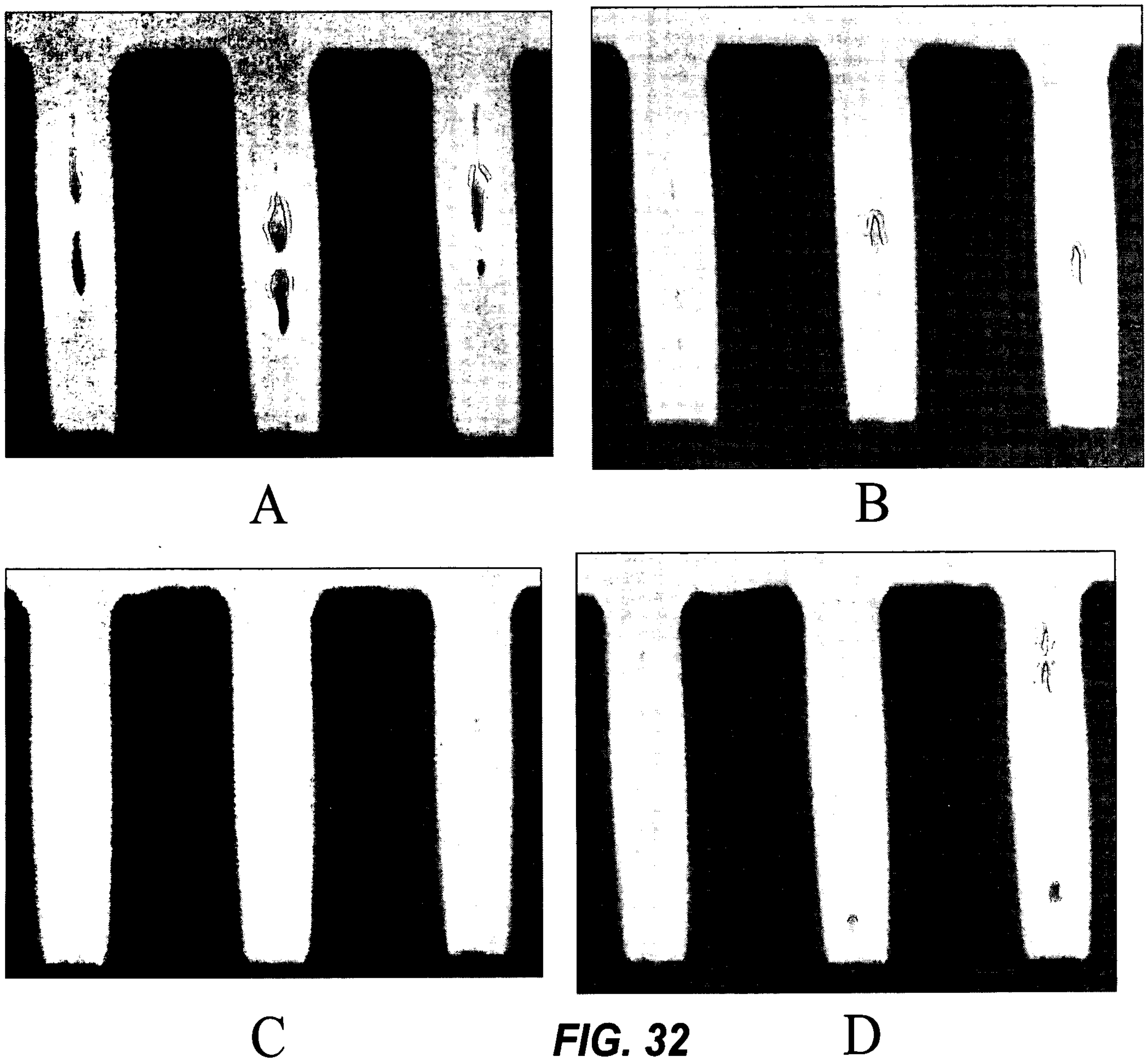


FIG. 32

•***Feature***: SEMATECH Standard vias, Field 5, **0.34 μm, AR = 4.5**
•***Seed***: 1600Å HCM Cu/250Å HCM Ta
•***Plate***: Step 1: 0.25A DC, 50 sec
Step 2: Pulse

Pulse Matrix

#	Ic	t_c/t_a ratio	Freq (Hz)	Toff
A	*4*	*49*	10	*0*
B	*4*	*49*	10	*3*
C	*8*	*25*	10	*0*
D	*8*	*25*	10	*3*

Reverse pulse matrix:

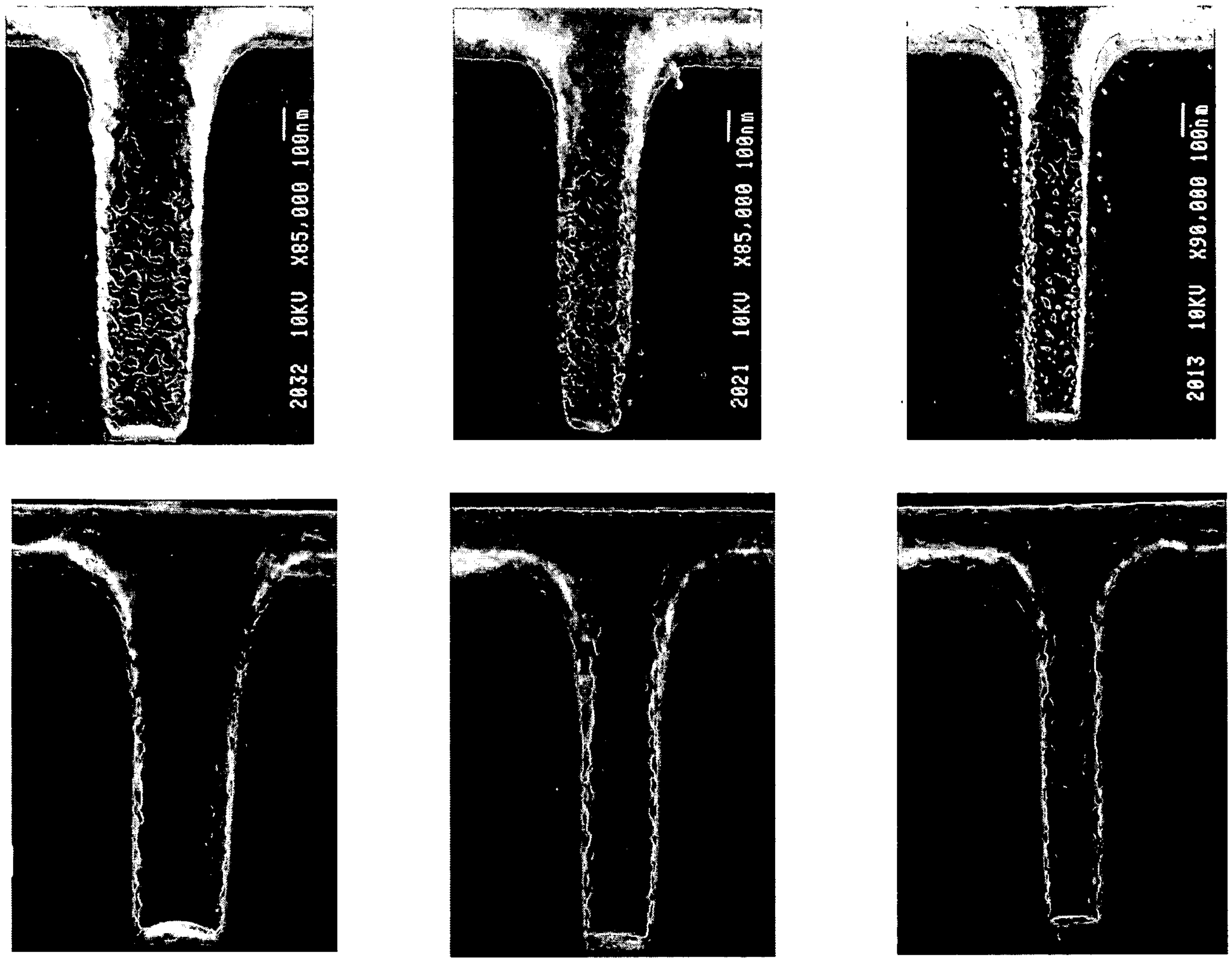
- **Reverse pulse shows superior fill compared to DC alone**
  - Low current initiation necessary
  - Smallest features filled (0.34μm, 4.5 AR)
- **Initial data indicates longer reverse pulse time yields better fill**
- **100 Hz clearly shows poorer fill than 10 Hz**

  Off time impact not clear
- **5:1 AR Via structure breakpoint**
  - Initiation limit-cannot overcome seed deficiency
  - Observed in backfilled via fill (Field 4, 0.21μm, 5:1 AR) also

Center voids eliminated on wafer edge and center by reverse pulse plating

FIG. 33

HCM vs. IMP Seed Comparison on Backfilled Vias



Note: 300 Å Ta + 2400 Å Cu

FIG. 34

Current Sweep Experimental Matrix #1

Experiment Number	Initial Current (A)	Maximum Current (A)	Time to Max Current (s)	Time at Max Current (s)	Current Sweep (mA/sec)	Total Equiv. Deposition Thick (Å)
1	0.1	2	25	82	76	2511
2	0.1	4	75	9	52	2505
3	0.1	4	60	17	65	2521
4	0.1	2	60	64	32	2521
5	0.25	2	50	68	35	2538
6	0.25	4	90	0	42	2525
7	0.25	4	45	24	83	2529
8	0.25	2	90	45	19	2525

FIG. 35

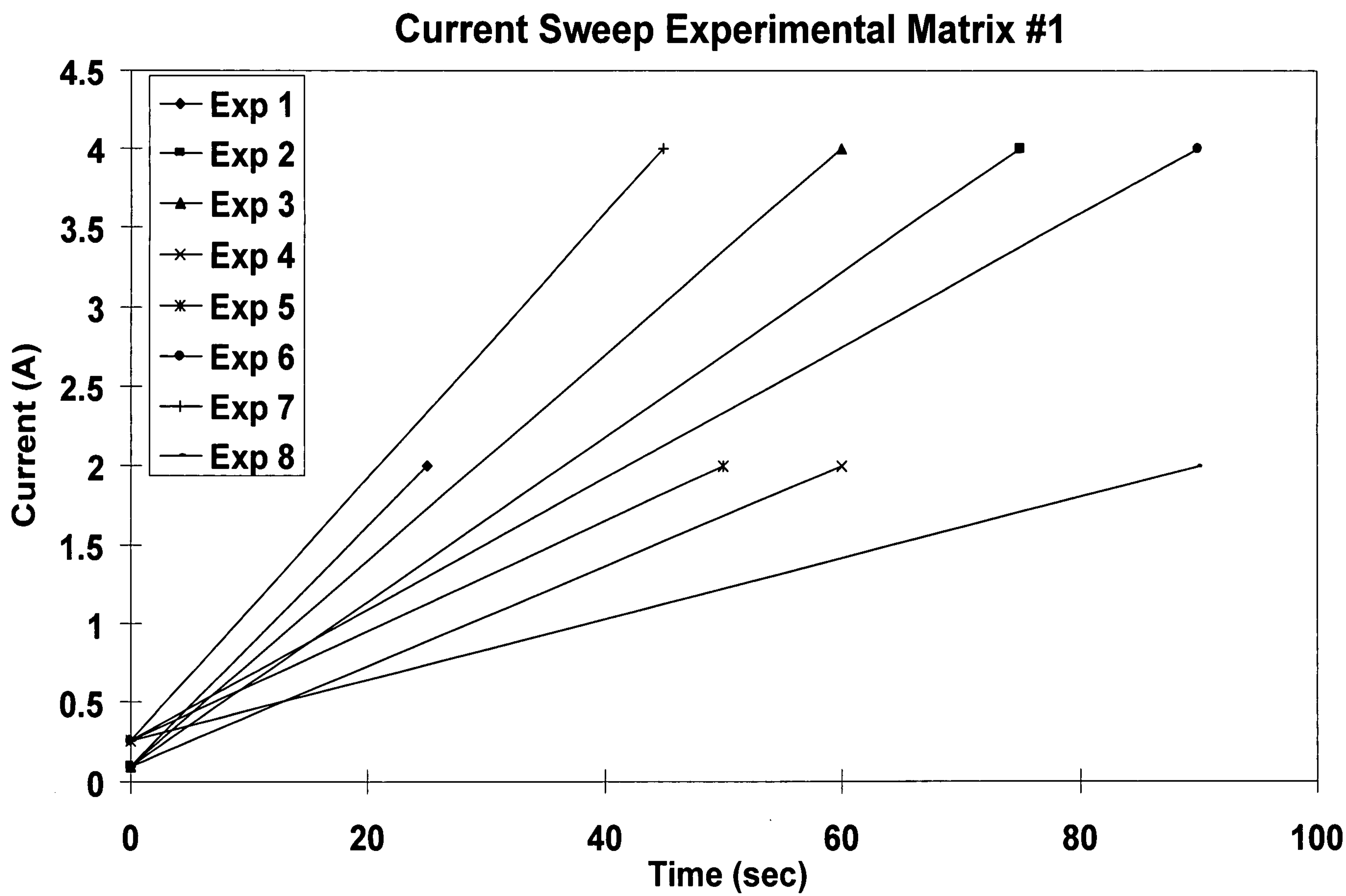

Current Sweep Experimental Matrix #1
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
Current (A)
Exp 1
Exp 2
Exp 3
Exp 4
Exp 5
Exp 6
Exp 7
Exp 8
0
20
40
60
80
100
Time (sec)

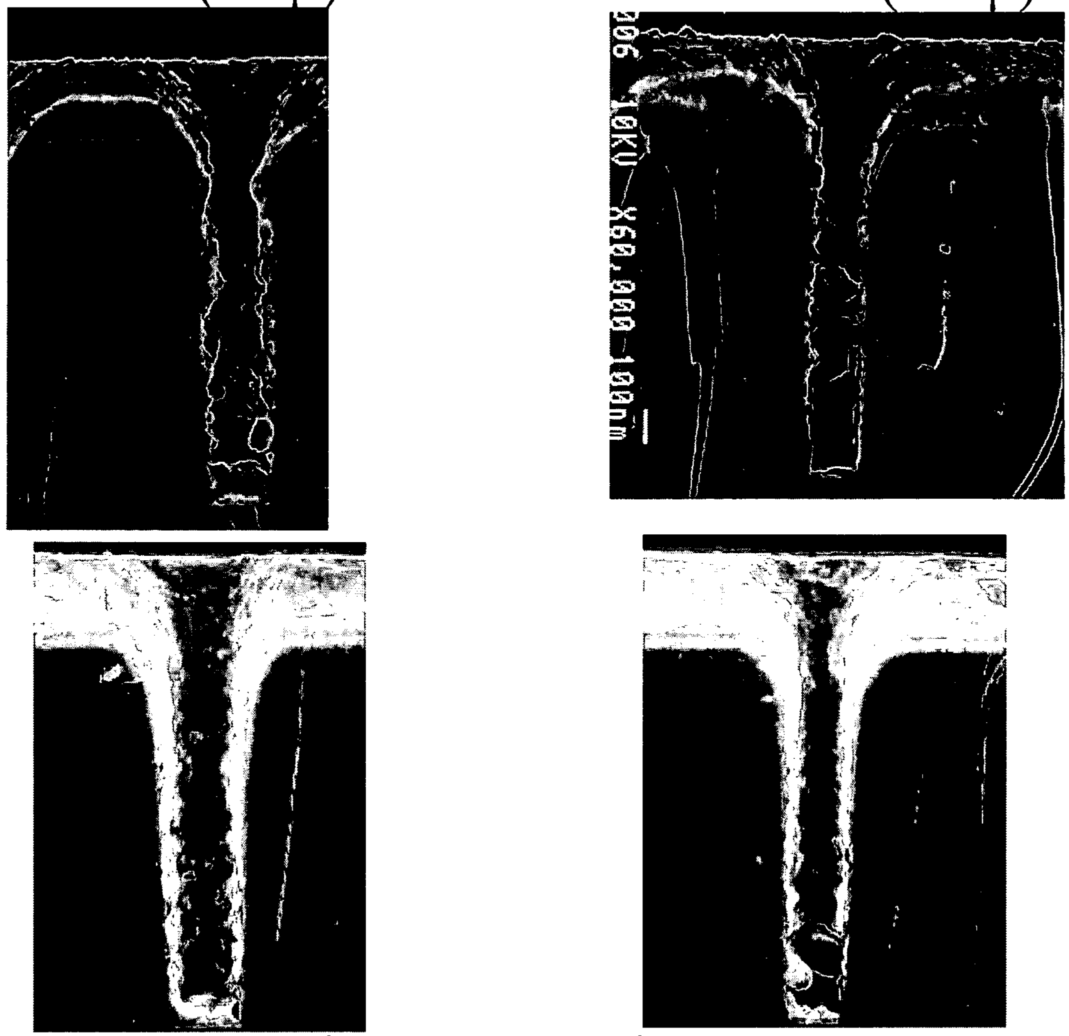
FIG. 36

Comparison: .5 Amp to .1 Amp Initiation

Field 3 (.25μ) | Field 4 (. 21μ)

.1 A
100s

.5 A
22.5s



Note: HCM POR6, 300 Å Ta + 2400 Å Cu

FIG. 37

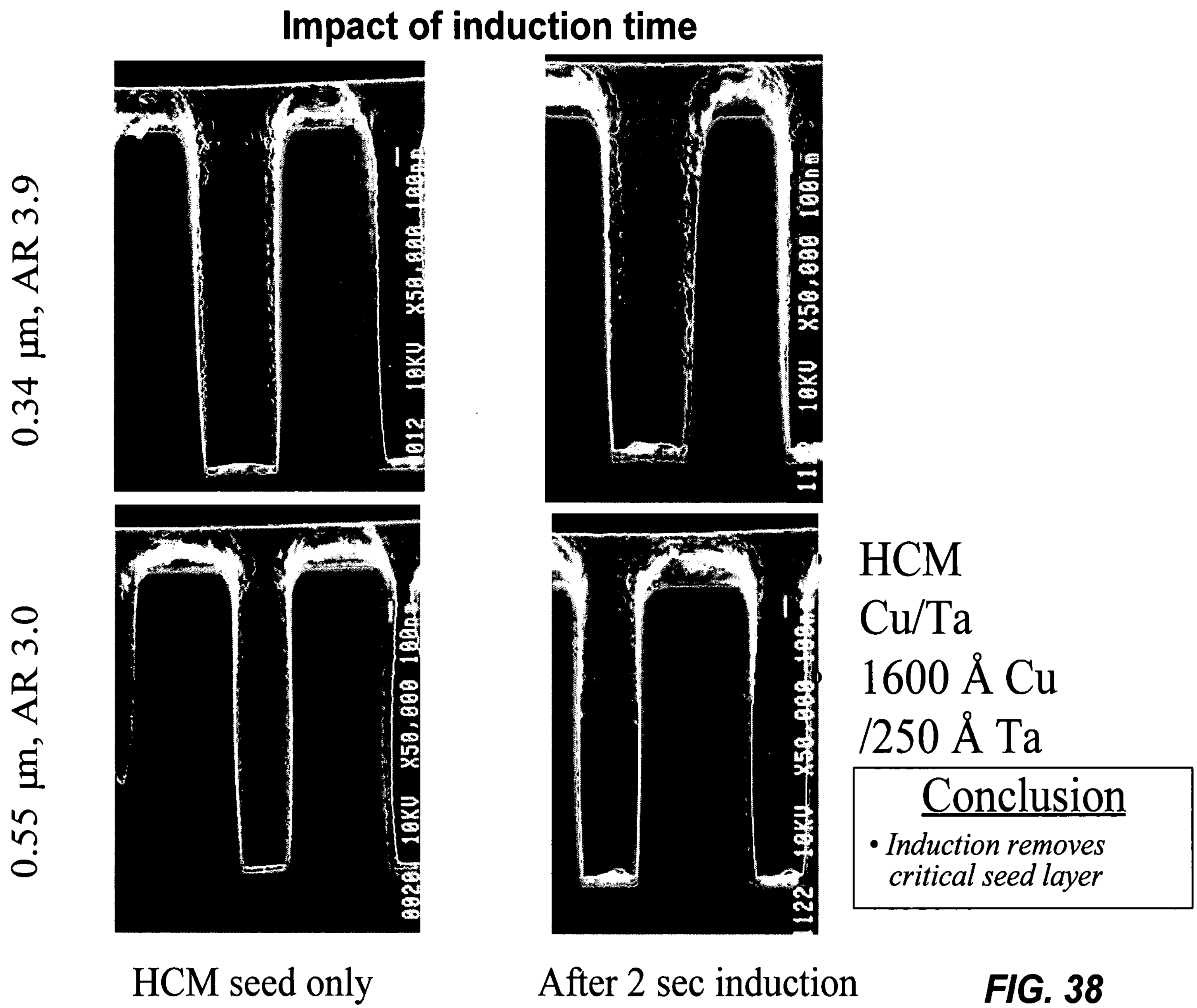

Impact of induction time
0.34 µm, AR 3.9
0.55 µm, AR 3.0
HCM seed only
After 2 sec induction
HCM
Cu/Ta
1600 Å Cu
/250 Å Ta
Conclusion
• Induction removes critical seed layer

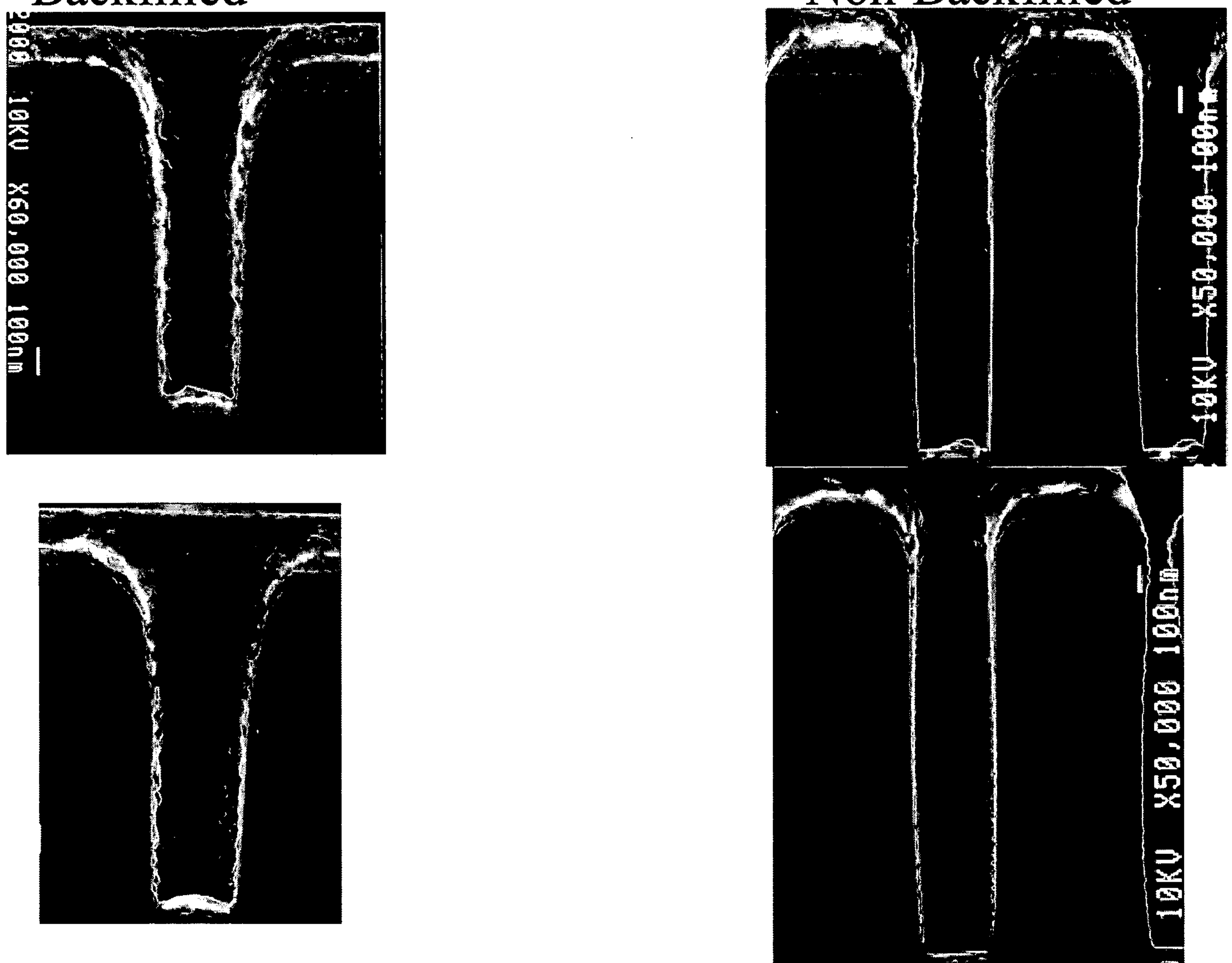
FIG. 38

Induction Comparison: Backfilled vs. Non-backfilled Vias

Backfilled | Non-Backfilled

2 sec Ind.

Seed Only



Note: HCM POR6 seed (2000-2400 Å), .3μ wide

FIG. 39

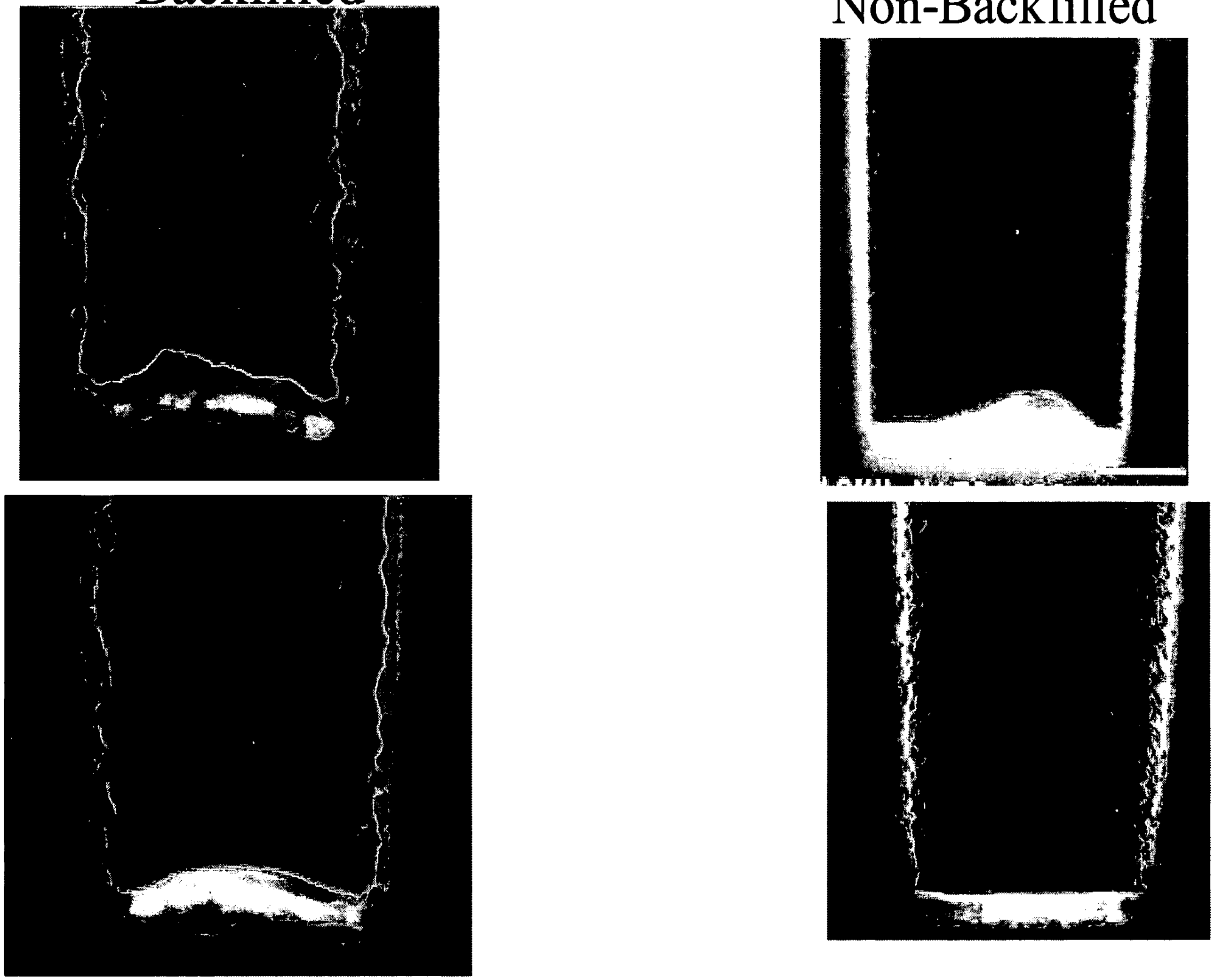
Induction Comparison: Backfilled vs. Non-Backfilled Vias

Backfilled

Non-Backfilled

2 sec Ind.

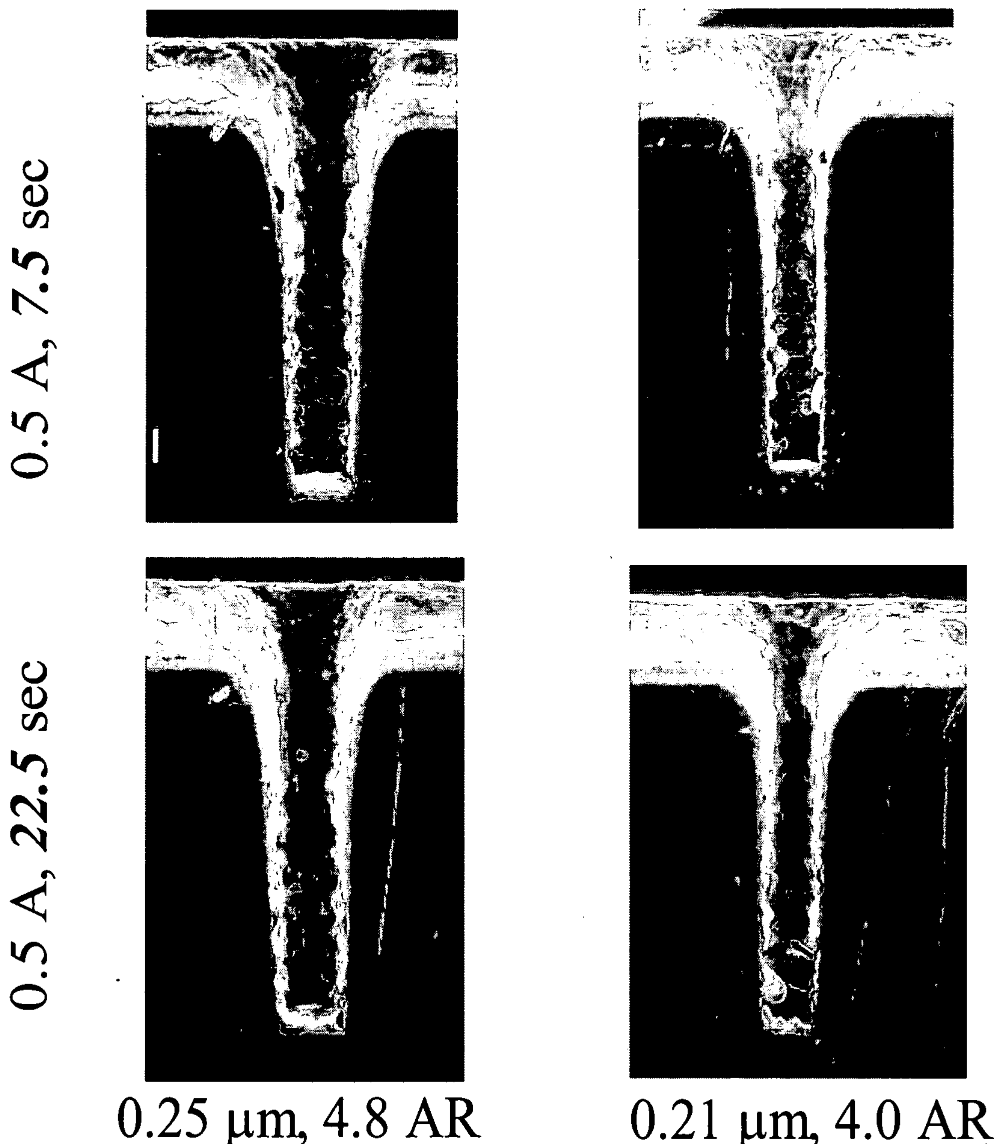
Seed Only



Note: HCM POR6 seed (2000-2400 Å), .3μ wide

FIG. 40

Initiation profile-Conformality



- HCM Cu/Ta
- 1600 Å Cu /250 Å Ta

Conclusion

- *Conformal growth even at small features*

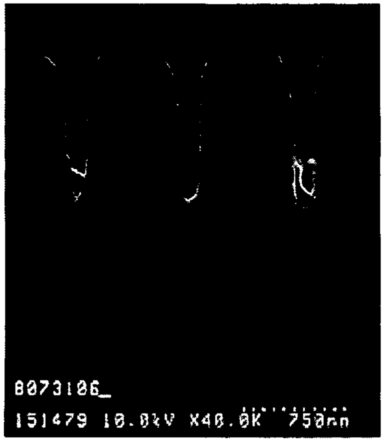
FIG. 41

Unipolar Pulse Tests: 0.18 μ Via Wafers

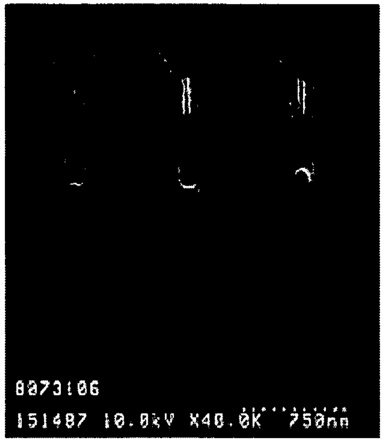
Wafer Id	Seed Thick	Induction Time	Initiation Time	Initation Conditions	Fill Time	Fill Current
3106-03	1600 Å	O seconds	8 seconds	5% 20 A 0.5A DC	15 seconds	7 A
3106-04	1600 Å	O seconds	8 seconds	2%, 50A 0.5A DC	15 seconds	7 A
3106-05	1600 Å	O seconds	16 seconds	5% 20 A 0.5A DC	15 seconds	7 A
3106-06	1600 Å	O seconds	16 seconds	2%, 50A 0.5A DC	15 seconds	7 A
3106-08	1600 Å	O seconds	16 seconds	5% 20 A	15 seconds	7 A

FIG. 42

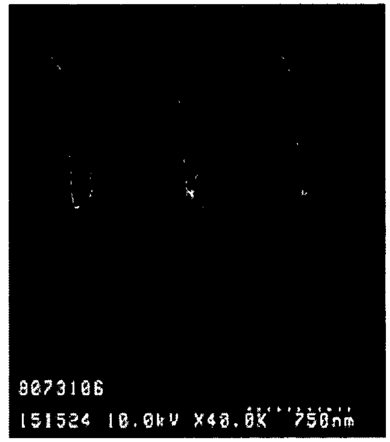
Unipolar Pulse = DC Initiation: Field 4



8 sec, 5% 20A



8 sec, 2% 50A



16 sec, 5% 20A

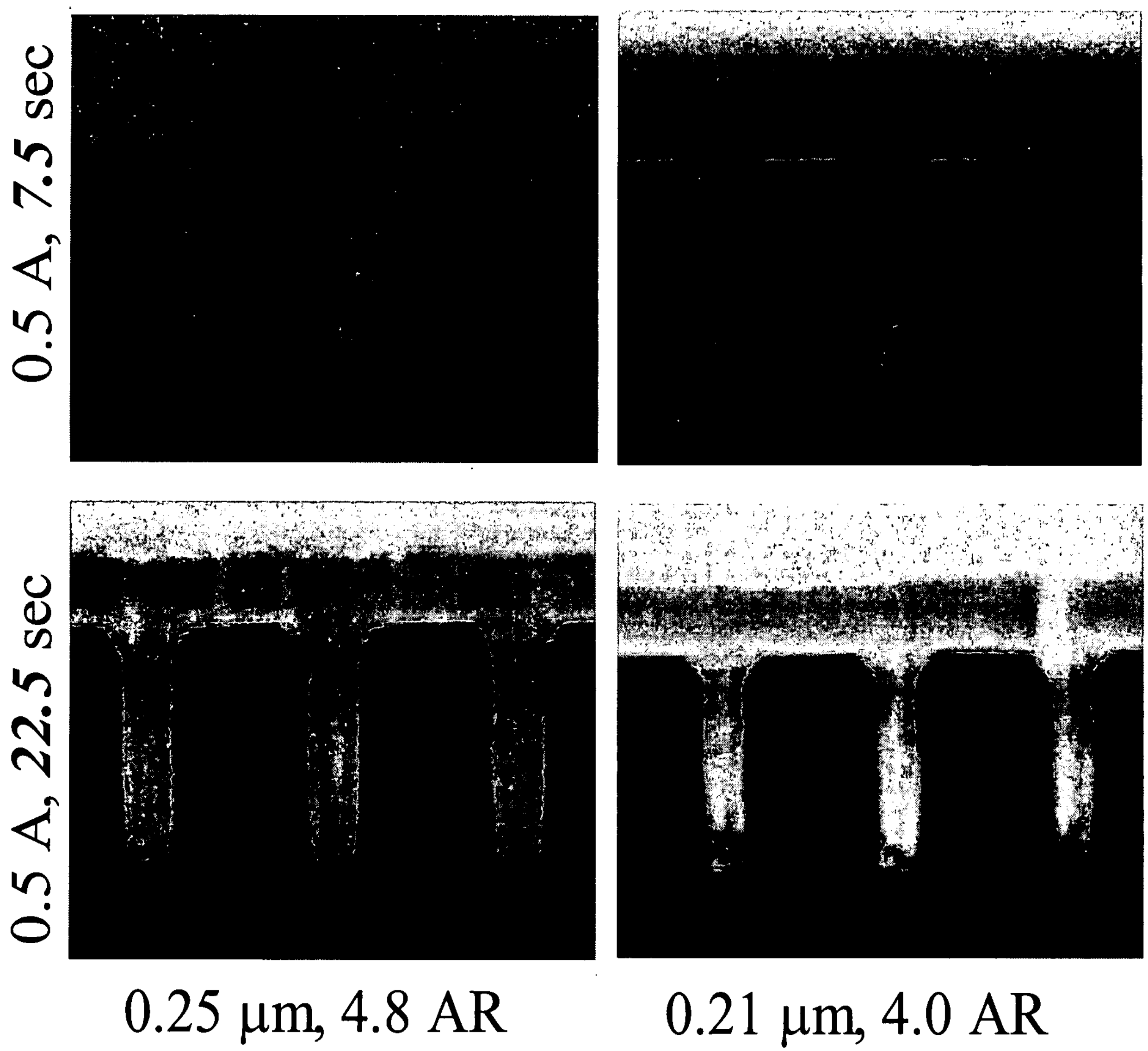
16 sec, 2% 50A

16 sec, 2% 50A
No DC background

-DC background current of 0.5A during initiation
-DC Fill of 7A for 15 seconds

FIG. 43

Initiation + Fill



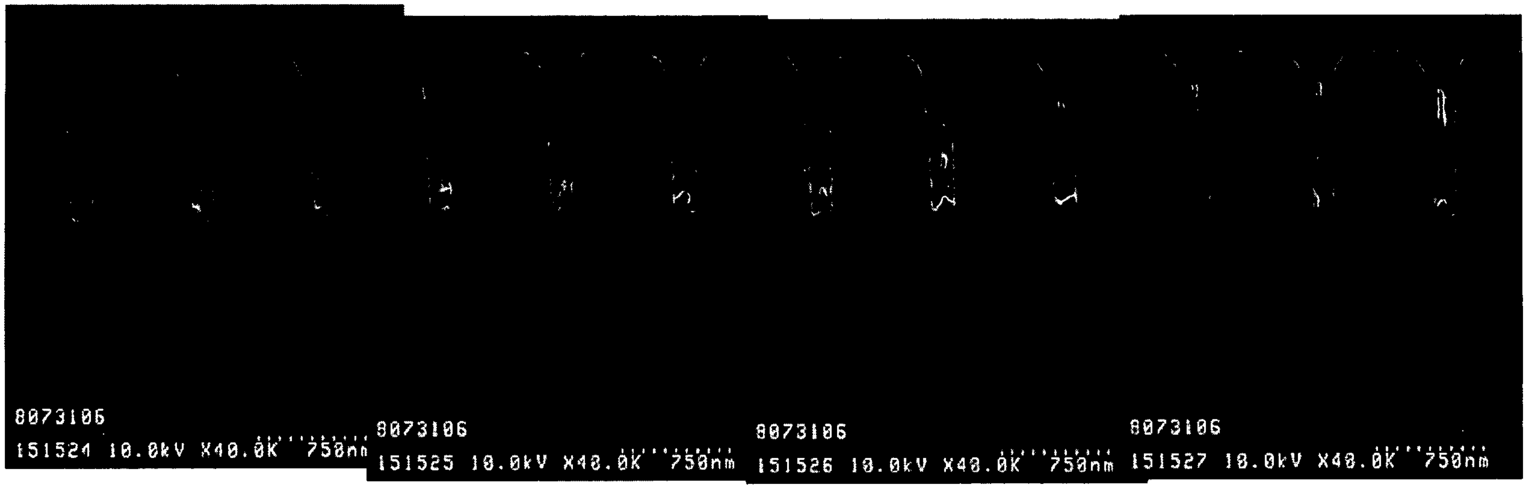
- HCM Cu/Ta
- 1600 Å Cu /250 Å Ta

Conclusion

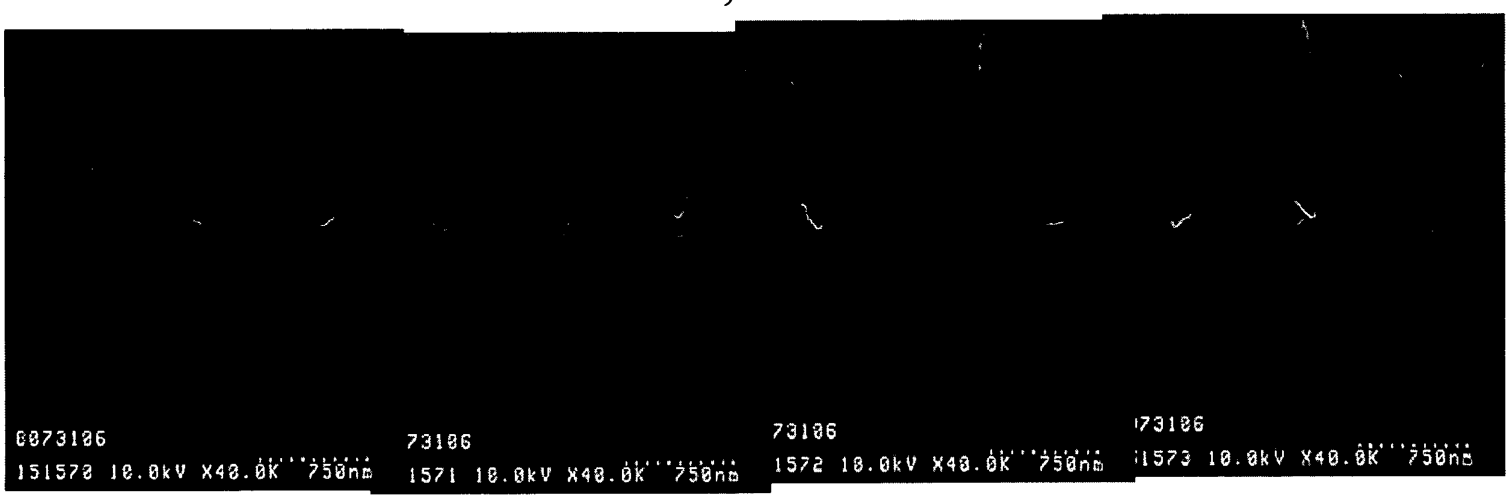
- *Initiation does not build seed at the bottom sidewall*
- *Correlates to final void formation*

FIG. 44

Comparison of 0.5 A Initiation: Unipolar Pulsing Conditions



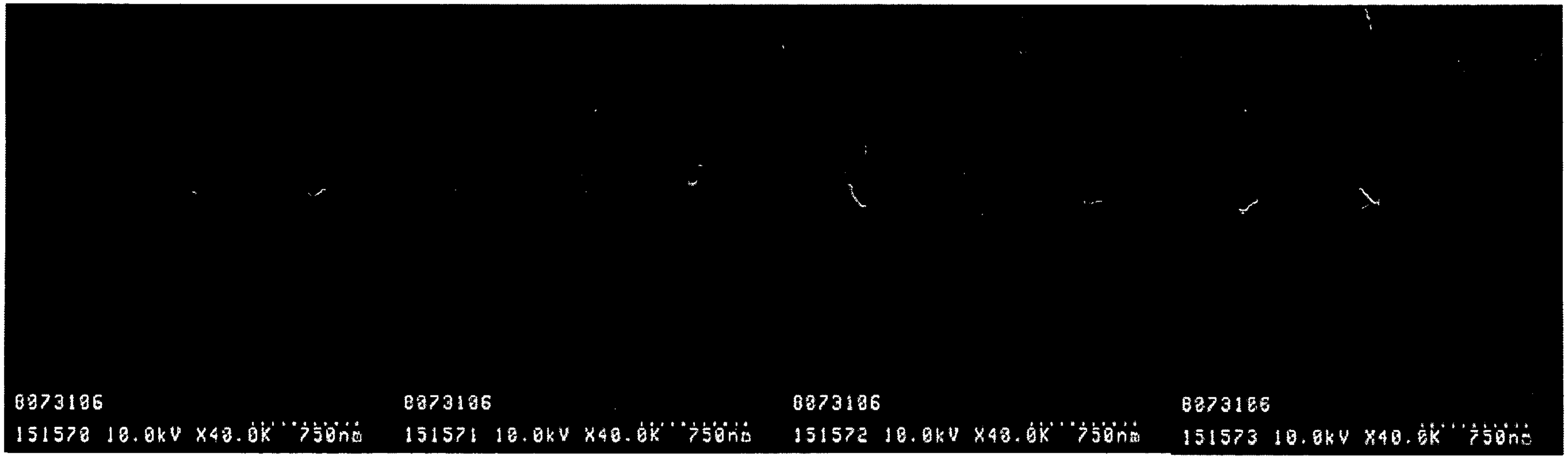
16 sec, 5% 20A



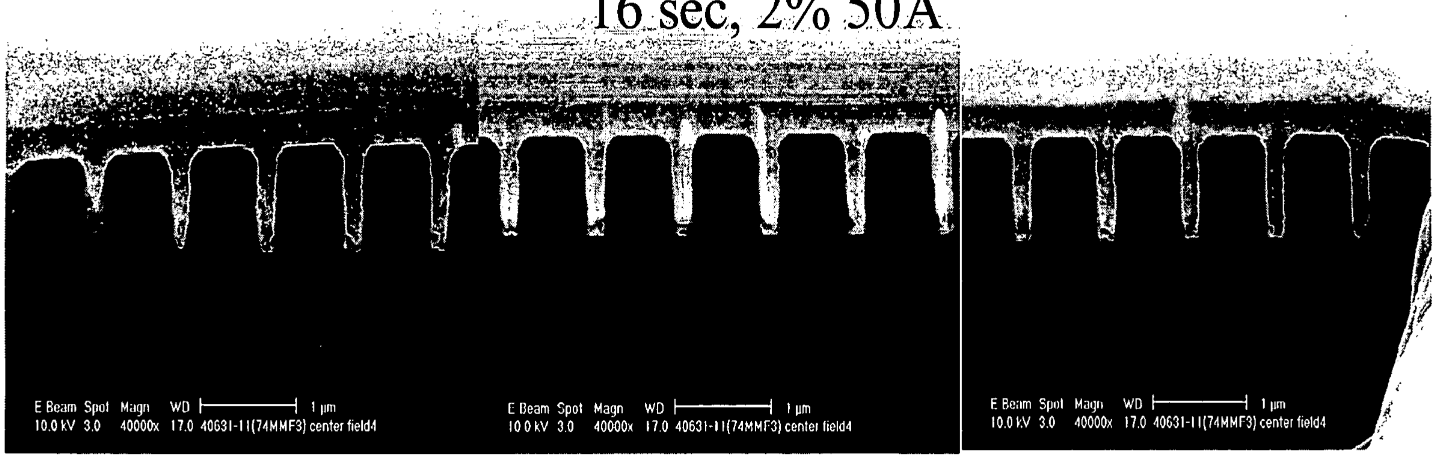
16 sec, 2% 50A

FIG. 45

Comparison of 0.5 A Initiation: With and Without Unipolar Pulsing



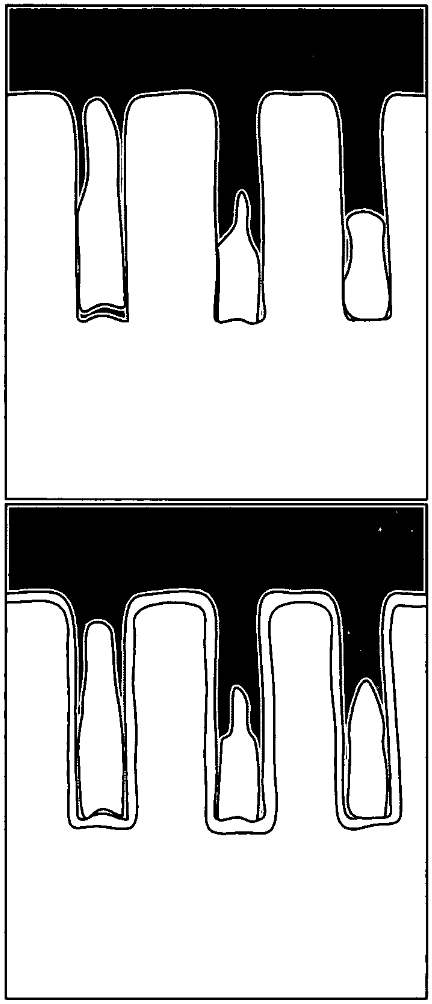
16 sec, 2% 50A



22 sec DC only

FIG. 46

Without Initiation: IMP seed:



- SEMATECH Backfilled via, Field 3, 0.24 μm x 1.13 μm, AR = 4.7
- Bottom Voids - Yes
- Side wall Voids - No
- Top Void - No
- Center Seam - No
- Film nucleation - poor
- Void % = 90%
- 2 second induction

Barrier/Seed Layer

-IMP
-250Å Ta/1600Å Cu
-Degas Temp.?
-Sputter etch thickness:?
-wafer bias:?

Electroplating

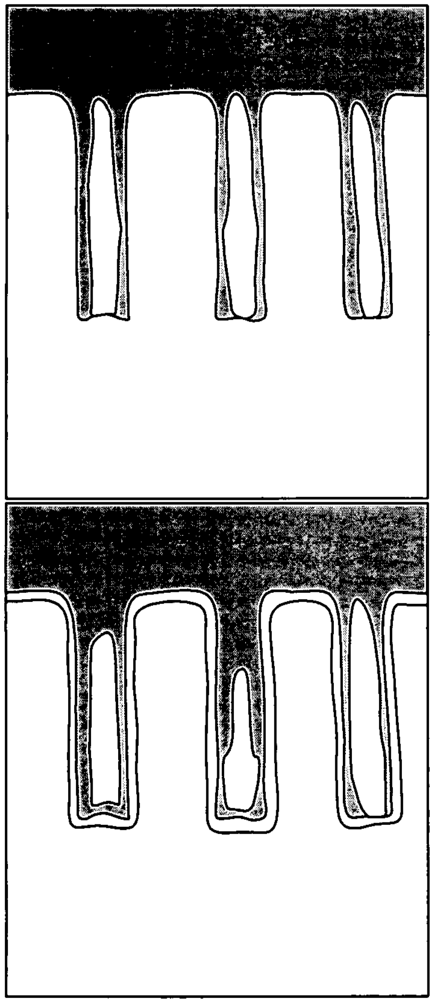
-DC, 7 A

Bath Conditions

$[Cu^{+2}]$ = 17.3 g/l	H_2SO_4 = 176 g/l
[MLO] = 3 ml/l	[MD] = 8 ml/l
$[Cl^-]$ = 55 ppm	Temp = 22°C
Flow = 8 lpm	RPM: 125

FIG. 47

Without Initiation: IMP seed:



- SEMATECH Backfilled via, Field 3, 0.24 μm x 1.13 μm, AR = 4.7
- Bottom Voids - Yes
- Side wall Voids - No
- Top Void - No
- Center Seam - No
- Film nucleation - poor
- Void % = 70%
- 2 second induction

Barrier/Seed Layer

-IMP

-250Å Ta/2200Å Cu

-Degas Temp.?

-Sputter etch thickness:?

-wafer bias:?

Electroplating

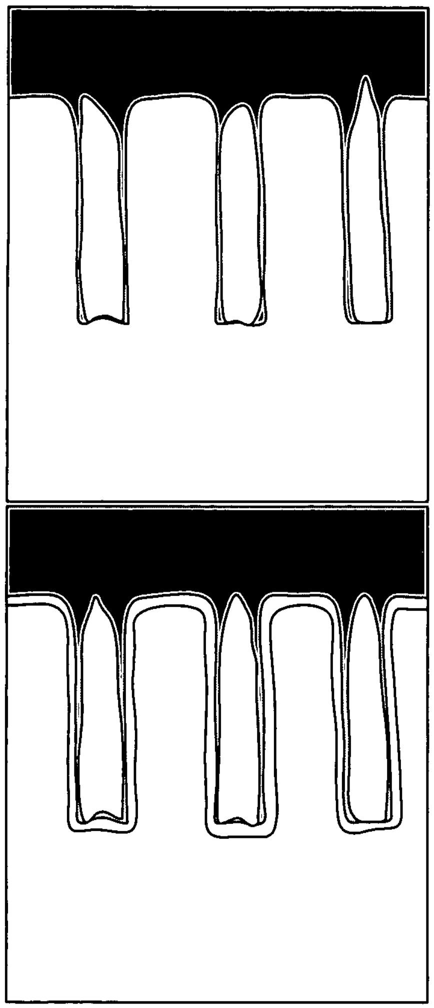
-DC, 1 A, 15 sec then 7 A

Bath Conditions

$[Cu^{+2}]$ = 17.3 g/l	H_2SO_4 = 176 g/l
[MLO] = 3 ml/l	[MD] = 8 ml/l
$[Cl^-]$ = 55 ppm	Temp = 22°C
Flow = 8 lpm	RPM: 125

FIG. 48

Without Initiation: IMP seed:



- SEMATECH Backfilled via, Field 2, 0.29 μm x 1.14 μm, AR = 4.0
- Bottom Voids - Yes
- Side wall Voids - No
- Top Void - No
- Center Seam - No
- Film nucleation - poor
- Void % = 90%
- 2 second induction

Barrier/Seed Layer

-IMP
-250Å Ta/1600Å Cu
-Degas Temp.?
-Sputter etch thickness:?
-wafer bias:?

Electroplating

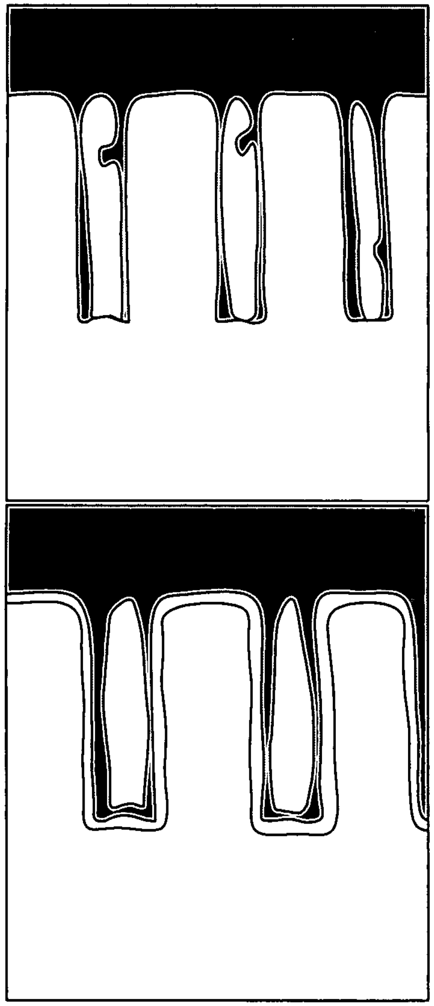
-DC, 7 A

Bath Conditions

$[Cu^{+2}]$ = 17.3 g/l	H_2SO_4 = 176 g/l
[MLO] = 3 ml/l	[MD] = 8 ml/l
$[Cl^-]$ = 55 ppm	Temp = 22°C
Flow = 8 lpm	RPM: 125

FIG. 49

Without Initiation: IMP seed:



- SEMATECH Backfilled via, Field 2, 0.29 μm x 1.14 μm, AR = 4.0
- Bottom Voids - Yes
- Side wall Voids - No
- Top Void - No
- Center Seam - No
- Film nucleation - poor
- Void % = 60%
- 2 second induction

Barrier/Seed Layer

-IMP

-250Å Ta/2200Å Cu

-Degas Temp.?

-Sputter etch thickness:?

-wafer bias:?

Electroplating

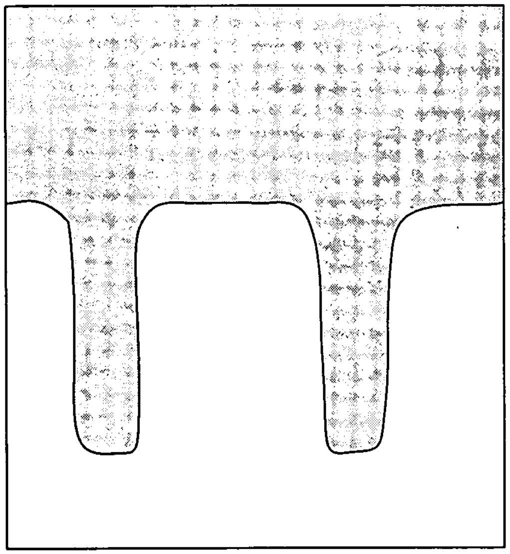
-DC, 1 A, 15 sec then 7 A

Bath Conditions

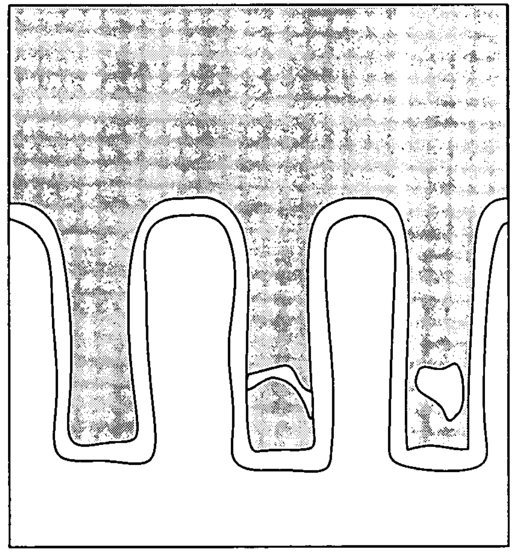
$[Cu^{+2}]$ = 17.3 g/l	H_2SO_4 = 176 g/l
[MLO] = 3 ml/l	[MD] = 8 ml/l
$[Cl^-]$ = 55 ppm	Temp = 22°C
Flow = 8 lpm	RPM: 125

FIG. 50

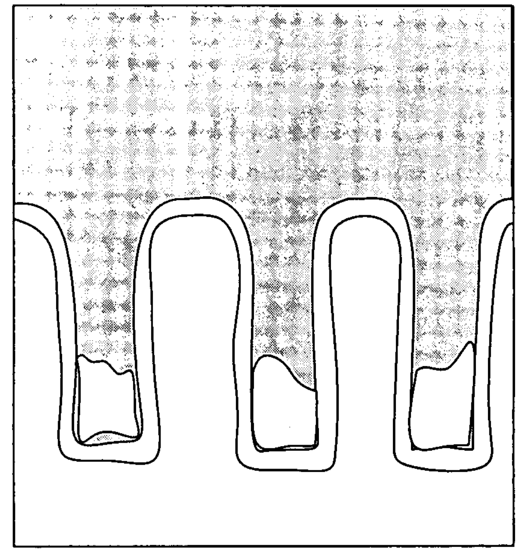
Initiation: Low current, 2 second induction



Field 2, 0.29 μm x 1.14 μm, AR = 4.0



Field 3, 0.24 μm x 1.13 μm, AR = 4.7
• Void % = 1.3%



Field 4, 0.2 μm x 1.0 μm, AR = 5.0
• Void % = 15.8%

- SEMATECH Backfilled via
- IMP Seed
- 250Å Ta/1600Å Cu

Electroplating

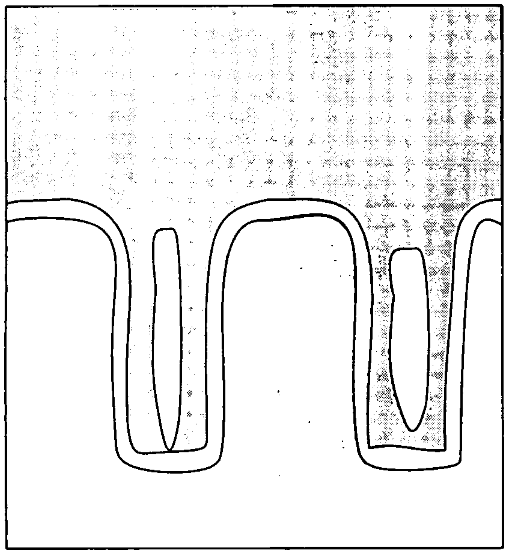
- Step 1: 1A for 15 sec
- Step 2: DC, 7 A

Bath Conditions

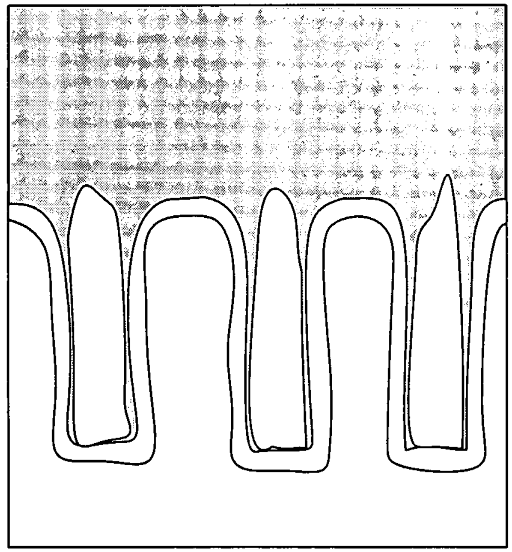
$[Cu^{+2}]$ = 17.3 g/l	H_2SO_4 = 176 g/l
[MLO] = 3 ml/l	[MD] = 8 ml/l
$[Cl^-]$ = 55 ppm	Temp = 22 °C
Flow = 8 lpm	RPM: 125

FIG. 51

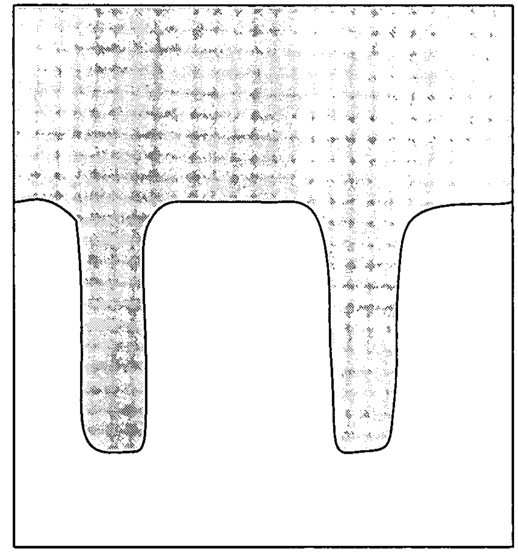
Initiation: Effect of Induction Delay



- DC, 7 A, 0 sec induction
- Void % = 16 %



- DC, 7 A, 2 sec induction
- Void % = 53 %



- Step 1: DC 1 A, 15 sec, 2 sec induction
- Step 2: DC, 7 A
- Void % = 53 %

- SEMATECH Backfilled via
- IMP Seed
- 250Å Ta/1600Å Cu

Field 2, 0.29 μm x 1.14 μm, AR=4.0

Bath Conditions

$[Cu^{+2}]$ = 17.3 g/l	H_2SO_4 = 176 g/l
[MLO] = 3 ml/l	[MD] = 8 ml/l
$[Cl^-]$ = 55 ppm	Temp = 22 °C
Flow = 8 lpm	RPM: 125

FIG. 52